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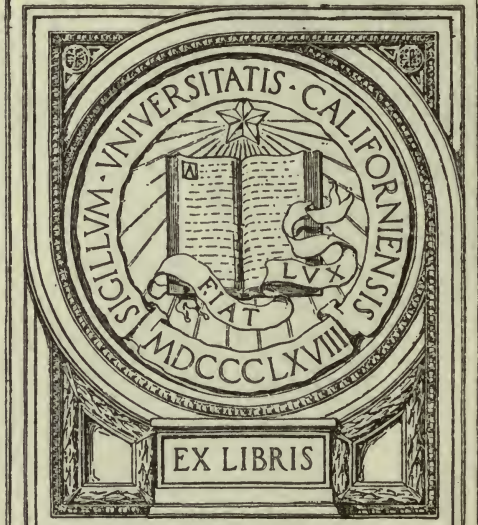

Gift

Thomas W. Huntington, Jr.

$HNO_3 \rightarrow \begin{matrix} H_2O \\ \{N_2O_5\} \end{matrix}$

$N_2O_5 + 2H = H_2O + 2NO_2$

$Zn + H_2S = \quad + \quad + S$

$Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O + 2NO_2$

$ZnS + HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2 + S$

nivalent	Bivalent	Trivalent	
1	2	3	The common
Na	All the rest	Cr	
K	Bivalent	Al	valence
NH4	chiefly	Fe	those in
Ag	(Fe)	(Mn)	brackets are
	Mn		the unusual
Hg)	(Hg)		valence

HNO_3 does not liberate H_2S in group I or II but S

A MANUAL OF CHEMICAL ANALYSIS

Acetates all soluble

Nitrates " "

Chlorides - Ag Cl, $Pb Cl_2$, Hg_2Cl_2 not Hg Cl, all others soluble

Sulphates - Ba, $CaSo_4$ Pb insol, bol sol

Carbonates all insolu except Na K NH_4

Phosphates " " " " " "

Hydroxides " " " Ba Ca Sr " " "

Chromates " " " Ca " " "

Sulphides " " " Ba Ca Sr " " "

Fe_2 not easily acted on remainder soluble in acids

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LONGMANS, GREEN, AND CO.

NEW YORK, LONDON, AND BOMBAY

A MANUAL

OF

CHEMICAL ANALYSIS

QUALITATIVE AND QUANTITATIVE

BY

G. S. NEWTH, F.I.C., F.C.S.

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ASSISTANT-EXAMINER IN CHEMISTRY, SCIENCE AND ART DEPARTMENT

NEW EDITION

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PREFACE TO THE SECOND EDITION

In bringing out this second edition of my "Manual of Chemical Analysis" so soon after its publication, I have acted upon the suggestion of one of my courteous reviewers, and have added to the short chapter on Physico-chemical Determinations a description of the "Freezing-point" and "Boiling-point" methods for determining molecular weights. With the exception of this addition, and the correction of certain errors and misprints incidental to a first edition, the book remains unaltered. I would take this opportunity to thank those friends who have kindly drawn my attention to such errata.

G. S. N.

June, 1899.

7922

PREFACE

A MAN once brought his son to the Royal School of Mines—now the Royal College of Science—with the request that he might be taught to "*do copper*." He did not want his boy to "*waste his time learning about oxygen and hydrogen, and all that*," but he wished him simply to learn to "do copper."

Although seldom expressed with such refreshing candour, the desire to *do analysis* without learning more than the minimum amount of chemistry is still very prevalent; and, unfortunately, chemical analysis is a subject which may be, and frequently is, taught and practised in such a manner as to degrade it to the level of a purely mechanical and often quite unintelligible series of rule-of-thumb operations.

I hope that the student whose aspirations rise no higher than to learn to *do analysis* in this fashion, will not find this book suitable for him. I have done my best to make it as little of a cram-book as possible, but have endeavoured to teach *analytical chemistry* as well as analysis—that is, the theoretical as well as the practical side of the subject.

With this object in view, I have carefully avoided the use of those symbolic abbreviated expressions (*slang formulæ*, they might be termed), such as $H_2\bar{O}$ (oxalic acid), $H_2\bar{T}$ (tartaric acid), $H\bar{A}$ (acetic acid) etc., which are becoming so common, and which, so far as the student is concerned, foster those very evils of cramming which we as teachers are striving to combat. If such symbols as these are permitted and recognised, why not $H_2\bar{S}$, $H\bar{N}$, $H_3\bar{P}$, for sulphuric, nitric, and phosphoric acids respectively? And then, perhaps, some such hieroglyphic as $H_2\hat{S}$, $H\hat{N}$, for sulphurous and nitrous acids.

For the busy chemist to make use of such shorthand signs in the privacy of his own note-books is one thing, but to print them in

a text-book intended for the learner, and thereby put them on the same footing as such chemical formulæ as H_2SO_4, $H_2C_2O_4$, etc., is quite another thing, and is open to the taunt of *chemistry made easy*.

The importance to the student of making careful notes of his analytical work while in progress, cannot well be overrated, as, perhaps more than anything else, this is calculated to develop in him those habits of exact observation which are essential qualities in a scientific man. While insisting on this point more than once, I have purposely refrained from giving anything of the nature of a *specimen of notes*, because notes which are made according to a stereotyped pattern are practically of no value. Unfortunately, it is the custom in most laboratories—perhaps a necessary custom, but none the less unfortunate—to require from the student some written account of his analysis by way of proof that he has conscientiously done the work. The result of this is that the notes which he makes are taken primarily with a view to furnish this required evidence. Points which ought to be observed and noted, points which he does not at the time understand, are passed over, while others which are familiar, and which are at once recognised as *useful evidence*, are written down. Indeed, as every teacher has experienced, the *evidence* is often more or less fabricated after the completion of the analysis.

The consequence of this method is the stereotyped product so painfully familiar to all who are engaged in teaching or examining, namely, a certain number of regulation tests, arranged with a semblance of method in the everlasting three columns, headed *Experiment*, *Observation*, *Inference*, followed by a more or less slovenly copy of the time-honoured tables.

The valuelessness of such a written-out record must be patent to all teachers, and yet we still continue to accept it in lieu of a few *real* notes, less quickly and easily examined no doubt, because less stereotyped, but of infinitely more value to the student himself.

In order to gain as much space as possible for purely anaytical matter, and still to be able to include within the limits of a convenient volume, both qualitative and quantitative analysis, I have carefully excluded all merely descriptive details which have no direct bearing upon analysis. For example, none of the properties, either chemical or physical, of such metals as those of the alkalies or alkaline earths, are made use of in ordinary analytical processes for the detection or recognition of these elements, therefore any

descriptive account of their properties in the elemental state is entirely out of place in a book which is intended only to teach *analytical* as distinguished from *general* chemistry.

In the second portion of the book, devoted to quantitative analysis, I have confined myself to a comparatively small number of well-tried typical methods and processes, preferring to describe and explain in tolerably full detail, a few quantitative determinations in each of the various sections, such as shall furnish a thoroughly sound course of practical study, rather than to attempt to cover—necessarily in more sketchy outlines—a wider range of subjects. Whether the choice of processes and examples I have made is as good or as representative as it might be, will no doubt be a matter for difference of opinion, and as the book has not been written to meet any particular syllabus, this is probably a point upon which hardly any two teachers will exactly agree.

The illustrations throughout have been made from original photographs of the actual apparatus employed in the various analytical operations described.

G. S. N.

Royal College of Science, London,
June, 1898.

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CHEMICAL ANALYSIS

BOOK I.

QUALITATIVE ANALYSIS.

CHAPTER I.

PRELIMINARY EXERCISES.

THE first step that the student must take in approaching the subject of analytical chemistry, is that of making himself *practically* familiar with certain simple operations or manipulations which he will constantly be required to carry out in the course of his work, and upon the dexterous and cleanly performance of which much of his success as an analyst will depend. If he has not had previous experience in practical chemistry, therefore, he should carefully go through the following exercises.

1. **Filtration.**—The method by which a liquid is separated from any solid substance with which it is mechanically mixed, is most usually that of filtering the mixture through porous paper, known as *filter-paper*.

EXERCISE 1.—Fold a circular filter-paper into half, and then at right angles into half again. Open this into a cone having one thickness of paper on one side and three on the other. This cone is then placed in a glass funnel of such a size that the glass will project slightly *above* the paper. The paper is then moistened with distilled water, which should not be poured out of the funnel again, but allowed to run through. After being cautiously pressed into the glass funnel, the paper should fit close to the glass all round, leaving no air-spaces. If this is not the case, either another funnel of the right angle (60 degrees) should be selected, or another filter-paper folded so that the cone shall be of the same angle as the funnel. This can be done by making the *second* fold of the

paper *not* quite at right angles to the first. In this way a cone will be formed having either a more acute or more obtuse angle than 60 degrees, as the paper is opened out one side or the other. The funnel is supported by a metal or wooden stand.

Now place some diluted hydrochloric acid in a small beaker, and stir into it, by means of a glass rod, a quantity of finely powdered charcoal. When thoroughly mixed, pour upon the filter. When *slowly* pouring from a wide vessel like a beaker, there is risk of some of the liquid being spilt by running down the outside of the vessel, as shown in Fig. 1. If it be poured *quickly*, it is

FIG. 1.

FIG. 2.

likely to splash over the funnel. To prevent both of these accidents, the liquid should be poured down against a glass rod held lightly against the edge of the beaker, and in such a position that the liquid does not strike at once against the apex of the paper cone (Fig. 2).

The *filtrate* (*i.e.* the liquid which passes through the filter) may be received in another beaker, which should be placed close against the stem of the funnel, so that the liquid shall run down against the glass. In this way splashing is prevented. The filtrate should be perfectly clear, the whole of the solid being retained on the filter. When all the liquid has passed through, the charcoal and the filter-paper are both still soaked with the hydrochloric acid. In order to remove this, and so to make the separation of the solid from the liquid complete, the filter and its contents must be washed

with distilled water.* This is done by directing a fine stream of water from a wash-bottle into the funnel, working downwards from the upper edges of the paper, and so washing the charcoal down into the apex of the filter (Fig. 3). Each washing must be allowed to drain right through before more water is used. This must be continued until the filtrate is entirely free from acid, which may be ascertained by allowing one or two drops of it to fall upon a piece of blue litmus paper.

In practice, the size of the filter should bear a rational relation to the quantity of *solid* matter to be separated from a liquid. This is more especially important when the material retained upon the filter has to be washed. If the amount of solid is small, the filter used should be proportionately small, and the washing operation will be more quickly and effectually accomplished than if an unduly large filter is employed.

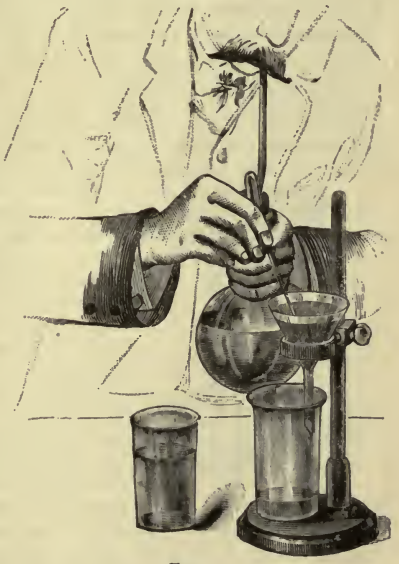

FIG. 3.

2. **Solution.**—This term is applied both to the *act* of dissolving and to the *product obtained* by dissolving.

EXERCISE 2.—Place a little powdered potassium carbonate in a test-tube, and add a small quantity of water. In a few moments the salt will have entirely dissolved. The salt has undergone *solution* in water. The product is *a solution* of potassium carbonate. The water is called the *solvent.* The process of solution is accelerated by heating the liquid, and it takes place more quickly the more finely the solid is powdered.

Put a similar quantity of potassium carbonate into another test-tube, and add a little dilute nitric acid. The salt again undergoes *solution*, the acid here being the solvent. But in this case there is a radical difference. First, a *visible* difference, in that the

* In the following exercises, and in all analytical operations, distilled water must always be employed; and when beakers, test-tubes, etc., are washed up after use, they must be finally rinsed with distilled water.

act of solution is accompanied by an effervescence, or rapid evolution of gas; and second, an *invisible* difference; for the resulting liquid *is not a solution of potassium carbonate, but of potassium nitrate.* In the first case, the process is not accompanied by any chemical change; the operation is therefore called *simple solution:* the original substance is present in the liquid, and can be obtained in its former state by evaporating the water. In the second case, the process is distinguished as *chemical* solution, because chemical action took place between the substance dissolved and the solvent, and the original substance cannot be got back by evaporating the solvent.

3. **Evaporation.**—The process of changing from the liquid to the gaseous or vaporous state is known as *evaporation.* This operation is greatly accelerated by the application of heat. When it takes place without the aid of external heat, the process is spoken of as *spontaneous evaporation.*

EXERCISE 3.—Pour the two solutions obtained in Exercise 2 into separate porcelain evaporating-dishes, and heat them gently by means of a Bunsen with a "rose" burner (as shown in Fig. 4). Continue the operation until all the liquid has evaporated away and a dry residue is left. This is called *evaporating to dryness.* As the condition of *dryness* is approached, the flame must be turned down more and more, to prevent the substance from "sputtering." Try to conduct the operation so that as little as possible of the residue is lost in this way.

FIG. 4.

The two residues may now be examined by one simple test, which will prove that the one from the watery solution is the same as it was before being dissolved, and that the other is quite different. Add to each a few drops of dilute nitric acid: the first dissolves with effervescence, as did the original potassium carbonate; the other is unacted on by the acid.

Sometimes it is necessary to carry on the operation of evaporation more carefully than can be done by heating the dish in the manner described. In this case the process is conducted upon a steam-bath. Water is boiled in a metal vessel (resembling a saucepan), and the evaporating-dish, supported by a metal ring which forms the cover, is heated by the steam. The following exercise is a case in point.

EXERCISE 4.—Dissolve some crystals of ammonium nitrate in a little water; place half the solution in a dish, and evaporate it

over a rose burner. Evaporate the other portion in a dish upon a steam-bath. Note the difference in the results in the two cases.

4. **Fusion** is the term used to denote the process of changing a substance from the solid to the liquid state by the action of heat. Thus, when lead is heated it *enters into a state of fusion*, or, shortly, it *fuses* or *melts*. Fusion must not be confounded with solution. Chemical action often takes place when one of the reacting substances is in a condition of *fusion*, which is incapable of taking place when they are only in *solution*. For example—

EXERCISE 5.—Dissolve a small piece of potassium hydroxide (*caustic potash*) in water, and add to the colourless solution a minute quantity of powdered manganese dioxide. No chemical action takes place.

Place a similar piece of potassium hydroxide in a dry test-tube, and heat it: the solid fuses to a colourless liquid. Drop into the fused mass a few particles of the manganese dioxide. Chemical action at once takes place, resulting in the formation of the deep green-coloured compound, potassium manganate. (This reaction is used as a test for manganese compounds.)

EXERCISE 6.—Place a *small* quantity of powdered barium sulphate in a test-tube, add water, and boil for a minute or two. If the amount of barium sulphate is *quite small*, it will be easy to *see* that practically none of it dissolves. Allow it to settle, and pour a few drops of the liquid upon a watch-glass, and set it to evaporate to dryness on a steam-bath.

Treat another similar quantity of the barium sulphate with dilute hydrochloric acid, and evaporate a few drops of the liquid in the same way. The result of these two operations will prove that *barium sulphate is insoluble in either water or hydrochloric acid.*

Next dissolve a little sodium carbonate in water, and add to the clear solution a few particles of barium sulphate; boil the liquid, and observe that no change takes place.

Now carefully mix a small quantity of barium sulphate with about five times as much sodium carbonate; place the powder in a platinum crucible, supported on a pipe-clay triangle in the manner shown in Fig. 5, and heat strongly with a blowpipe. When the mass has been in complete fusion for a few minutes, allow the crucible to cool. Then place it on its side in a small beaker with a little water, and warm gently. The mass in the crucible will soon become disintegrated, some of it dissolving, while a part remains undissolved. Filter the liquid as in Exercise 1, washing the residue upon the funnel until the filtrate no longer restores the blue colour to reddened litmus paper. Now pour a few drops of dilute hydrochloric acid upon the residue on the filter, receiving the liquid which passes through in a fresh beaker or test-tube. Observe that effervescence at once takes place. But this residue cannot be sodium carbonate, because that salt, being soluble in water, has

been all removed ; neither can it be barium sulphate, for that compound has been shown to be insoluble in dilute hydrochloric acid. By the process of fusion, the sodium carbonate and barium sulphate underwent a chemical reaction, resulting in the formation of sodium sulphate and barium carbonate. The former salt, being soluble in water, was dissolved in that liquid along with the excess of sodium carbonate. The barium carbonate is insoluble in water, but dissolves in dilute hydrochloric acid, forming barium chloride (soluble) and carbon dioxide, which escapes as gas. Therefore, by fusion the *insoluble barium sulphate is converted into soluble barium carbonate.*

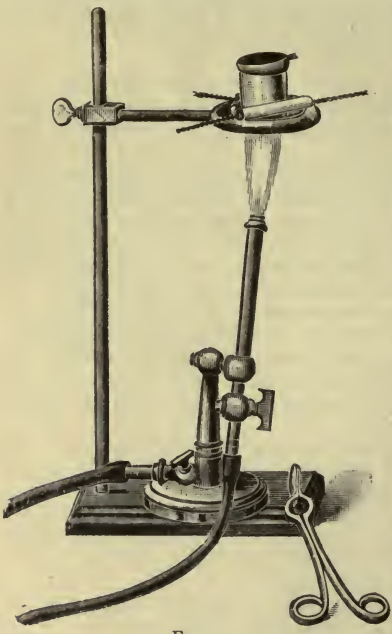

Fig. 5.

5. **Precipitation.**—When chemical action takes place between substances in solution, and one of the products of the action is insoluble, the latter substance is thrown out of solution, or *precipitated.* The substance so thrown down is termed a *precipitate.*

Exercise 7.—Dissolve a minute quantity of sodium chloride (common salt) in water in a test-tube. In another tube dissolve a small crystal of silver nitrate, and mix the two solutions together. The two compounds react upon each other, forming sodium nitrate (soluble in water) and silver chloride (insoluble in water). The insoluble white *precipitate* is therefore the silver chloride.

If, in the above example, the two substances are mixed in a *particular* proportion, there may have been *exactly* the amount of sodium chloride necessary to supply chlorine enough to unite with the *whole* of the silver in the silver nitrate used. In this case there would be nothing left in *solution* but sodium nitrate, *i.e.* no excess of either silver nitrate or of sodium chloride. Ascertain if this happened to be the case in Exercise 7, by the following experiment :—

EXERCISE 8.—Filter the mixture obtained above, and divide the filtrate into two portions. To one add a single drop of a solution of sodium chloride. (1) If a precipitate is formed, it proves that there is some silver nitrate present, and that therefore an *excess* of this compound was used in Exercise 7. Continue adding the sodium chloride solution one drop at a time,* shaking or stirring the liquid after every addition, so long as it produces further precipitation.

(2) If no precipitate is thrown down by adding sodium chloride, add *to the second portion of the filtrate* a single drop of silver nitrate solution. If this gives a precipitate, it proves that sodium chloride is present, and that therefore an *excess* of this substance had been employed in Exercise 7. Continue adding the silver solution drop by drop, with constant stirring, so as to hit off as nearly as possible the exact point when it just ceases to produce any further precipitate.

The exact point at which precipitation is complete is not equally easy to determine in all cases. Some precipitates are heavy, granular, or crystalline, and settle quickly ; others again are light or flocculent, and only subside slowly and imperfectly, so that it is difficult to see whether the addition of more of one of the solutions does or does not produce any additional precipitate. In such cases the liquid should be filtered, and the filtrate tested by adding a few drops more of the precipitant.

Very often several substances present together in one and the same liquid, form insoluble compounds with another which is added. These will not be all precipitated simultaneously, but in a certain order one after the other, the precipitation of one being more or less complete before that of the next begins. The substance being added, first selects the compound present for which it has the greatest chemical affinity, and afterwards that with which it unites less eagerly. This being so, it will be evident that unless care be taken to ensure *complete* precipitation, it might easily happen that the *whole* of one of the substances present in the solution escaped precipitation. It is of the utmost importance, therefore, in analysis, to be quite sure that precipitation is as complete as possible. On the other hand, the reckless addition of precipitants is a fault which must be as carefully guarded against, as it is almost as fruitful a source of trouble as the other.

In most instances, also, it is essential to wash the precipitate until it is quite free from any of the soluble substances present in

* When solutions are to be added drop by drop, it is best to use a pipette ; that is, a piece of ordinary glass tube drawn to a point at one end, and about 6 or 8 inches long.

the liquid, as explained in Exercise 1. A precipitate may be removed from the filter either by means of a spatula (preferably platinum, but, failing this, either glass or porcelain; iron should never be used), or by pushing a glass rod through the apex of the filter, and then washing the precipitate through by means of the wash-bottle, or by dissolving it off by pouring into the funnel the liquid to be used for its solution.

EXERCISE 9.—Add a solution of sodium carbonate to a solution of barium chloride, until precipitation is just complete. Barium carbonate is precipitated, and sodium chloride remains in solution. Pour the mixture upon three separate filters, and wash the precipitate on each until quite free from sodium chloride (see Exercises 7 and 8), getting the precipitate well down into the apex.

Take the first filter, and remove a portion of the precipitate with a spatula. If the quantity in the funnel is small, then carefully draw the paper cone out of the funnel, spread it open upon a flat sheet of glass, and scrape off as much of the precipitate as possible with the spatula, and transfer it to a test-tube. Dissolve it by adding a few drops of hydrochloric acid.

Through the apex of the second filter push a glass rod, and wash the precipitate through into a test-tube, using a fine jet of water, and as little of it as possible. Dissolve this also by adding a few drops of the same acid.

Upon the third filter pour a small quantity of hydrochloric acid, collecting the filtrate in a test-tube. Pour the filtrate back over the precipitate once or twice, until the whole has dissolved.

6. **Ignition.**—Strictly speaking, this word carries with it the idea of combustion. In common speech it signifies the act of "setting fire" to an inflammable substance; and in more scientific language we speak of the *ignition temperature*, or the *igniting-point* of a body, meaning thereby the temperature, to which it is necessary to raise it in order that combustion may be initiated. Unfortunately, in analytical phraseology the term *ignition* is used in a somewhat slipshod way to denote a variety of operations where substances are simply strongly heated, and where the idea of combustion is altogether excluded. In this book the words *heat* or *strongly heat* will be used instead of *ignite* to signify these operations.

EXERCISE 10. *Strongly heating in an open dish.*—Place a little solution of ammonium chloride in a small evaporating-dish, and evaporate to dryness. Then strongly heat the dish with the dry residue until no more white fumes (consisting of the volatilising ammonium chloride) are evolved. If the dish has been heated all over, there should then be nothing left in it. The complete vaporisation of the salt is more quickly and certainly accomplished

by using a small platinum capsule or crucible in which to heat the residue obtained by evaporating the solution to dryness.

EXERCISE 11. *Strongly heating in a tube closed at one end.*—Place a minute quantity of mercuric oxide in a small test-tube (4 inches × $\frac{5}{16}$), and apply heat to the compound. Note the change of colour.; also that it gradually disappears, and that a *sublimate* collects on the cool part of the tube, having a white metallic appearance. Test the evolved oxygen by means of a glowing splint of wood. By means of a paper "spill" rub the metallic sublimate, and (if necessary, with a pocket lens) see the globules of mercury.

EXERCISE 12. *Heating in the blowpipe flame.*—Select a piece of small tubing of *lead glass*, and heat it in a blowpipe flame, holding the glass in the *extreme tip* of the flame until it is red hot. Then gradually bring it further into the flame, and observe that when the glass reaches the *inner cone* of the flame a film begins to appear upon the red-hot portion. On withdrawing the glass to the tip of the flame again, this film gradually disappears. Bring the glass once more into the inner cone of flame, and when the film has again made its appearance, remove the glass and allow it to cool. It will then be seen that what appeared like a film when it was hot, is a black shining metallic-looking deposit in the glass. This deposit is *metallic lead.* The lead compound in the glass, when heated in the inner cone of flame, is *reduced* to the metallic state ; and when, after being so reduced, it is heated in the tip of the flame (*i.e.* in the outer cone or sheath of the flame), the metal is again oxidised. The inner flame is therefore called the *reducing flame*, and the outer cone is distinguished as the *oxidising flame.**

EXERCISE 13. *Heating on charcoal in the blowpipe flame.*—Select a close-grained piece of charcoal, as free as possible from cracks, and file a flat surface upon it with a broad, flat file.† On the flat part scoop a small hollow, and place in it a little red-lead mixed with about an equal quantity of sodium carbonate. Heat this mixture in the inner blowpipe flame, holding the blowpipe and the charcoal in the manner shown in Fig. 6, so that the flame shall play along the surface of the charcoal. Very quickly the lead oxide will be reduced to the metallic state, and appear in the form of brilliant silvery globules. When the charcoal is removed, it will be seen that surrounding the cavity there is a yellowish deposit, or incrustation. This consists of lead oxide. If the outer tip of the flame be directed upon this incrustation it will quickly disappear, and will impart a bluish colour to the end of the flame.

Pick out one or two of the globules of metal, and gently strike one with a small hammer, or with a pestle, upon some hard surface.

* The memory of the beginner may be aided by the alliteration, *O*uter, *O*xidising. The inner flame is a reducing agent by reason of the fact that within the cone there is an excess of strongly heated coal-gas ; whereas in the outer flame there is an excess of heated atmospheric oxygen.

† Specially prepared rectangular blocks of charcoal (6 inches long and 1 square inch section) are sold for the purpose. One such block can be used many times.

Note whether the metal is hard and brittle, or soft and malleable. Also further identify the metal as lead by rubbing it upon a piece of paper, which will be marked by it much as by an ordinary pencil.

EXERCISE 14.—Heat on another piece of charcoal a crystal or two of zinc sulphate with a little sodium carbonate in the inner blowpipe flame. No metallic globules are formed in this case, because zinc is too easily oxidised; but an incrustation appears on the charcoal, which is canary-yellow while hot, but turns white on cooling. Touch the incrustation with a single drop of a solution of cobalt nitrate, and again heat it, using the *outer* flame. The

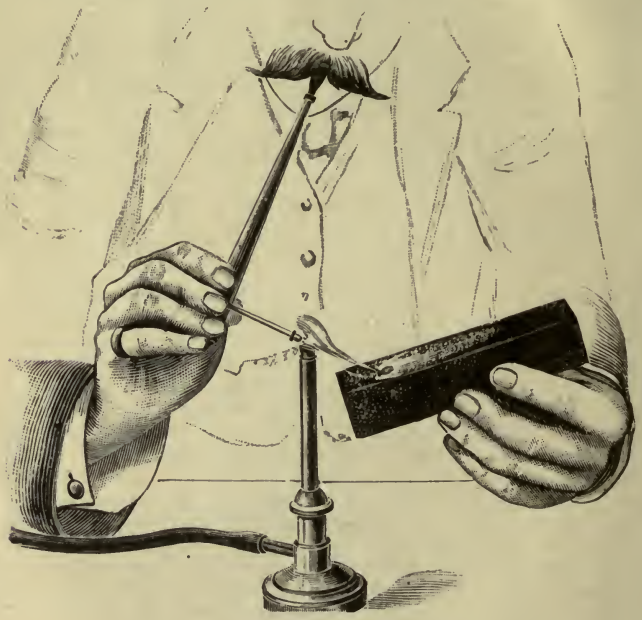

FIG. 6.

incrustation then becomes green. Notice that the incrustation is not driven off by being thus heated, because zinc oxide is not volatile.

7. **Fusion with Borax.**—When borax is strongly heated, it melts to a clear vitreous mass. In this condition it is capable at a high temperature of dissolving many metallic compounds, giving in some cases characteristically coloured glasses.

EXERCISE 15.—Twist the end of a piece of platinum wire into a small round loop or eye,* and pick up a little borax upon it by first heating the wire and then dipping it while hot into the powdered salt. On heating the borax upon the wire in a blowpipe flame, it first swells up, and finally fuses, forming a transparent colourless bead of borax glass. Allow the bead to cool, and touch it with a glass rod which has been dipped into a solution of any cobalt salt, so as to bring only a minute quantity of the cobalt compound upon the bead. Heat the bead once more, and notice that as it melts the borax loses its transparent appearance. When again allowed to cool, the bead will appear of an azure blue colour.

If too much of the cobalt salt was employed, the bead may appear almost black; in this case a part of it may be shaken off when it is fluid, and more borax picked up and melted with what remains of the original bead upon the wire. If too little cobalt is present, the colour will be correspondingly pale. The colour of the bead is best examined by holding it against a white object (such as the bottle of borax itself) in a good light.

Fuse the bead again, holding it first in the *outer* flame, and afterwards in the *inner* flame, and see that in each case when cold the blue colour remains the same.

EXERCISE 16.—Make another borax bead, and touch it with a small quantity of a solution of manganous sulphate. Heat this in the outer blowpipe flame. After cooling, examine the colour carefully. Pale violet, lilac, purple, or amethyst. Heat the bead again, holding it in the inner flame. Notice that it gradually loses its opacity; that as it is heated, something in the fused mass which seems to give it an appearance of muddiness clears away, and the molten globule looks clear. When it is in this condition remove it, and when cold it will be found to have lost its colour entirely. Manganese compounds therefore give a purplish bead in the outer flame, which becomes colourless upon being heated in the reducing flame.

8. **Neutralisation.**—When an acid is carefully mixed with an alkali (the substances being in solution), a point is

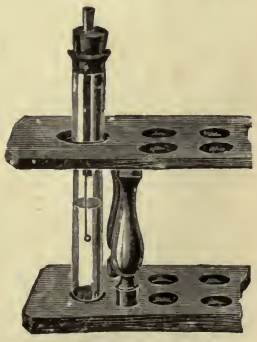

FIG. 7.

* For greater convenience, as well as economy, a short piece of wire (about 2 inches) should be fixed into a glass tube, about the same length, to serve as a handle. The glass tube is first drawn out to a point, and the wire inserted into the fine end. On bringing this into a blowpipe flame, the glass fuses round the wire and holds it. Two or three of these should be made, and a convenient plan is to fit the glass tube into a cork, so that when not actually in use the wires can be kept in small test-tubes containing dilute hydrochloric acid, as in Fig. 7.

reached when the mixture no longer possesses the properties of either the acid or the alkali. The solution is then said to be *neutral*. The point of neutrality is ascertained by the use of certain sensitive colouring matters which have their colour changed by acids and alkalies. The commonest of these is *litmus*, the solution of which in water has a purple colour, capable of being turned *red* by acids, and *blue* by alkalies. The yellow colour of turmeric is changed to brown by alkalies, but is not altered by acids, therefore this can only be used to indicate alkalinity, and will not discriminate between a neutral and an acid liquid.

EXERCISE 17.—Add a few drops of litmus solution to a little dilute hydrochloric acid in a beaker standing upon a piece of white paper, or a white tile. Add to the red liquid some solution of sodium hydroxide, adding it cautiously in small quantities, with constant stirring, until the colour of the litmus is *just* turned blue. The liquid is now *alkaline*. By means of a glass rod moistened with the dilute acid, introduce a minute additional quantity of the acid, so as to cause the colour of the litmus to become of a purple tint. The solution is then *neutral*, and the least trace of either acid or alkali will at once turn it red or blue, as the case may be. (Instead of adding litmus solution, papers tinted with litmus may be dipped into the liquid.)

All substances which redden litmus are not *acids*, although all acids will redden litmus. That is to say, there are many things which have an *acid* or *sour* taste which do not belong to that class of compounds which chemists call *acids*. An acid may be defined as *a compound containing hydrogen which can be displaced by a metal, when the latter is presented to it in combination as a hydroxide*. The hydrogen which is thus *displaced* is not liberated as free hydrogen, but unites with the hydrogen and oxygen of the metallic hydroxide to form water, while the metal takes the place of the hydrogen thus displaced from the acid.

CHAPTER II.

Analytical Classification.

The word *analysis*, in its strict meaning, signifies the breaking up or separation of a compound substance into its constituent parts. It is the true antithesis of the word *synthesis*, which means the building up of a compound from its constituents. For example, when an electric current is passed through a solution of common salt, the compound is split up or separated into its two component elements, sodium and chlorine. The operation is therefore "analytical." When sodium and chlorine are brought together under suitable conditions, the two elements unite, and reproduce the compound sodium chloride, the process in this case being a synthetical one.

But the word *analysis* has come to bear a wider meaning, and to include all the various processes and operations which chemists make use of in order to find out what any compound is composed of, or to enable them to identify the substance, quite irrespective of whether or not the process involves the breaking up of the body into its component parts. Thus, a chemist will often recognise a substance by its particular crystalline form, or from some other characteristic appearance it may present when examined under a microscope (*microscopic analysis*). Or sometimes he can detect the presence of certain elements in an unknown substance, by examining the light which is emitted when the compound is strongly heated (*spectrum analysis*).

Reactions.—Most analytical operations, however, involve some chemical change. These changes are called *reactions*. When the change is effected by strongly heating the substance, it is described as a *dry reaction*, or a *reaction in the dry way*. This is to distinguish this class of reactions from those which take place between substances that are dissolved, either in water or some other liquid, and which are sometimes spoken of as *wet reactions*, or *reactions in the wet way*.

Most analytical reactions are "double decompositions," in which one of the products of the chemical action is either markedly different from the others and from the reacting compounds, in its solubility, or its colour; or where it is evolved as a gas having properties by which it may be readily identified. For instance, the two compounds barium chloride and sodium sulphate are soluble in water, forming colourless solutions; if these are mixed together, "double decomposition" takes place, resulting in the formation of sodium chloride and barium sulphate, thus—

$$BaCl_2 + Na_2SO_4 = 2NaCl + BaSO_4$$

The barium sulphate is practically insoluble in water, and consequently is precipitated. Now, if we know some property belonging to this precipitate of barium sulphate which is so characteristic of the compound that we could thereby identify it and distinguish it from all other white precipitates, then this reaction between barium chloride and sodium sulphate can obviously be used as a means of testing for the presence of either a soluble *barium* salt or a soluble *sulphate*. For if, on adding a solution of sodium sulphate to an *unknown* solution, barium sulphate were precipitated, the unknown liquid must have contained a soluble barium salt; or, on the other hand, if we add barium chloride to an unknown solution and obtain barium sulphate again, then this unknown solution must have contained a sulphate.*

Reagents.—The materials that are used to bring about analytical reactions are termed *reagents*. Thus, in the illustration given above, the sodium sulphate is the *reagent* when it is added to the unknown solution in order to test for barium; while the barium chloride is the *reagent* when it is used to test for a sulphate. Some reagents are capable of causing reactions of a similar character with a number of substances; such are often known as *general* reagents. Others, again, are employed because they produce a characteristic reaction with some one substance in particular; these are distinguished as *special* reagents.

Reagents are the tools with which the analyst works, and upon the intelligent and skilful use of them everything depends. In most laboratories the student finds himself supplied with all the necessary reagents ready prepared; but for the help of those who may require to make them up, brief directions for doing so are given in the Appendix.

Analytical Classification.—Substances are usually divided

* Sulphuric acid being included, as hydrogen sulphate.

into two classes, namely, (1) *Metals*, and (2) *Acid-radicals.* These are also sometimes called *positive* radicals and *negative* radicals respectively. When analysing such a compound as sodium chloride, NaCl, the sodium and the chlorine are each separately detected: the sodium is the metal (or positive radical), and the chlorine is the acid (or negative) radical. But in such a case as sodium nitrate, $NaNO_3$, we do not separately detect the sodium, the nitrogen, and the oxygen, but the sodium and the negative or acid radical represented by the formula NO_3. Or, again, when such a compound as ammonium sulphate, $(NH_4)_2SO_4$, is submitted to analysis, we do not separately test for the elements nitrogen, hydrogen, sulphur, and oxygen, but for the positive radical NH_4, and the acid-radical SO_4.

Sometimes the radicals, whether metals or acid radicals, may be detected by being actually isolated, in which case they are recognised by their known properties in the free state. For example, from the compound lead chloride, $PbCl_2$, it is easy to isolate both the lead and the chlorine. The metal lead so obtained is readily identified by its familiar physical properties, while the gas chlorine is equally easily distinguished by its own well-known characteristics.

In some cases, where a radical is incapable of isolated existence, it may be detected by the separation of some product of its decomposition. Thus, in such a compound as ammonium carbonate, $(NH_4)_2CO_3$, neither the positive radical NH_4, nor the acid-radical CO_3 can exist in the free or uncombined state. But we detect the presence of the former by the evolution of ammonia, NH_3, and the latter by the expulsion of carbon dioxide, CO_2, from the compound.

In the large majority of cases, however, whether the various radicals are capable of isolated existence or not, they are detected by causing them to pass into fresh combinations with certain reagents, whereby new compounds are formed which are readily recognised by their known properties. Thus, in the case of sodium chloride above quoted, instead of isolating the chlorine, we can employ the reagent silver nitrate, $AgNO_3$. When this is added to a solution of sodium chloride, double decomposition takes place, and silver chloride, AgCl, is formed, which, being insoluble in water, is precipitated. Silver chloride has properties by which it is easily recognised, hence by the formation of this compound we can detect the presence of the chlorine in sodium chloride.

In analytical classification the term "metal" includes, besides

the metals proper, certain *metalloidal* elements, such as arsenic, selenium, and others (which, strictly speaking, are not true metals, but which lie on the borderland between the metals and the non-metals), and also the compound positive radical ammonium, NH_4. These "metals," then, are divided into a number of groups, based on the behaviour of their compounds towards certain reagents.

As, however, more than one scheme or plan of analysis is possible, due either to a different choice of reagents or to their use in a different order, so the analytical classification of the metals which is followed by some chemists varies somewhat from that used by others.

In this book the following arrangement will be adopted :—

Group I.	Group II.	Group III.	Group IV.	Group V.
Silver	**Mercury**	**Aluminium**	**Barium**	**Ammonium**
Mercury	**Lead**	**Chromium**	**Strontium**	**Sodium**
Lead *	**Bismuth**	**Iron**	**Calcium**	**Potassium**
——	**Copper**	**Nickel**	——	**Magnesium**
Thallium †	**Cadmium**	**Cobalt**		——
Tungsten	**Antimony**	**Manganese**		Lithium
	Arsenic	**Zinc**		Rubidium
	Tin	——		Cæsium
	Gold	Beryllium		
	Platinum	Zirconium		
	——	Thorium		
	Ruthenium	Cerium		
	Rhodium	Scandium		
	Palladium	Yttrium		
	Osmium	Lanthanum		
	Iridium	Ytterbium		
	Tellurium	Titanium		
	Selenium	Tantalum		
	Molybdenum	Niobium		
		Uranium		
		Indium		
		Thallium		
		Vanadium		

In the regular course of analysis, the groups are separated in the order in which they are here numbered. The "silver, lead, mercury" group is separated first, and the "ammonium, sodium," etc., group last. In studying the reactions of the metals, however,

* The reason why certain metals are placed in more than one division will appear later.

† The substances printed in small type are usually called *rare* elements.

it is more usual to begin with the *fifth* group, for the reason that the compounds of these metals are less complex, and the student is therefore led on gradually from what is comparatively simple to that which is more difficult. Because of this, some chemists prefer to number the groups in the reverse order, that is, in the order in which the *preliminary study* of them is made, instead of the order in which they are actually disposed of in the course of analysis.

The reagents by means of which the elements are separated into these groups, and which are known as *group reagents*, must be used in regular order. Each is only capable of separating its own family of metals from those *coming after it* in the series, and *not* those going *before*. For example, the group-reagent for Group II. is only capable of separating the metals of this family from those of III., IV., and V., but not from those of Group I. If, therefore, the metals of Group I. are not first separated, they may be precipitated along with the members of the second family by the group-reagent for that family.

The various group-reagents (or general reagents) and the particular compounds of the metals which are precipitated by them are indicated in the following table :—

GROUP I. — *General reagent*, **Hydrochloric acid, HCl,** precipitates

AgCl, $Hg^{I}_{2}Cl_2$, $PbCl_2$ (partially soluble).
($TlCl$, H_2WO_4.)*

GROUP II.—*General reagent*, **Sulphuretted hydrogen, H_2S,** precipitates in acid solution

(*a*) **PbS, $Hg^{II}S$, Bi_2S_3, CuS, CdS** (Ru_2S_3, Rh_2S_3, PdS, OsS.) } Insoluble in ammonium sulphide.

(*b*) **Sb_2S_3, As_2S_3, $Sn^{II}S$ and $Sn^{IV}S_2$, AuS, PtS_2** (Ir_2S_3, TeS_2, Se, MoS_3.) } Soluble in ammon. sulphide.

GROUP III.—*General reagent*, **Ammonium sulphide, $(NH_4)_2S$,** precipitates in presence of ammonium chloride and ammonia

(*a*) Hydrated compounds { **$Al_2(HO)_6$, $Cr_2(HO)_6$.**
($Be(HO)_2$, $Zr(HO)_4$, $Th(HO)_4$, $Ce(HO)_3$, $Sc(HO)_3$, $Y(HO)_2$, $La(HO)_3$, $Yb(HO)_3$, H_2TiO_3, H_3TaO_4, H_3NbO_4.)

* The compounds represented by the formulæ in small type are those of the so-called *rare* elements. They are included in the table in order to give, in a bird's-eye view as it were, not only their *position* in the scheme of classification, but also the composition of their compounds, which are precipitated by the group-reagents.

(*b*) Sulphides { **FeS, NiS, CoS, MnS, ZnS.**
(UO_2S, InS, Tl_2S) (*Vanadium* converted into soluble ammonium thiovanadate *).

GROUP IV. — *General reagent*, **Ammonium carbonate, $(NH_4)_2CO_3$**, precipitates in presence of ammonium chloride and ammonia

$BaCO_3$, $SrCO_3$, $CaCO_3$.

GROUP V. — *No general reagent.* The group consists of **(NH_4), Na, K, Mg.** (Li, Rb, Cs.)

* Vanadium belongs to the "arsenic and antimony" family in the *natural* classification of the elements. The sulphide is, however, not precipitated by H_2S, V_2O_5 being thereby reduced to V_2O_4, which gives a blue colour to the liquid. NH_4Cl, in presence of ammonia, precipitates white ammonium metavanadate, NH_4VO_3, but ammonium sulphide converts this into the soluble ammonium thiovanadate, which gives a brown colour to the solution. The true group-reagent, therefore, does not actually precipitate this metal.

CHAPTER III.

Reactions of the Metals of Group V.

This group contains the alkali metals (ammonium being regarded as a metal), and also the element magnesium, which is more nearly allied to the metals of the *alkaline earths*. The members of this family are not precipitated by any group-reagent, but they are (with the exception of ammonium) separately tested for in the solution which is obtained after the metals of Groups I. to IV. have been removed. By referring to the table on p. 17, it will be seen that, in the course of separating the various groups, certain ammonium compounds are employed, therefore it will be obvious that it is necessary to test for this "metal" in the substance under examination *before* adding any ammoniacal compounds.

Ammonium, NH_4.

Dry Reactions.—When heated alone in a glass tube, ammonium salts undergo change.

(*a*) If the acid is readily volatile, the salt dissociates, but the ammonia and the volatile acid, as they together pass away from the heated area, immediately reunite, reproducing the original compound, which then settles or condenses on the cool part of the tube, forming a *sublimate*.

[Generally, however, a certain small amount of the dissociated portions of the compound escapes recombination : *e.g.* heat a small quantity of ammonium chloride in a dry test-tube ; notice that white fumes are produced, which sublime up the tube. Now hold a moistened red litmus paper in the mouth of the tube, and it will be turned blue, showing that a *portion* of the ammonia escapes from the tube before it meets the hydrochloric acid from which it has been dissociated. For a moment discontinue heating, and presently the blued paper will be reddened, for the molecules of hydrochloric acid which have lost their partners (the escaped ammonia) now make their way up the tube and act on the litmus paper.]

(*b*) If the acid is non-volatile, or volatile only at a high temperature, then the ammonium salt is decomposed, ammonia being evolved, while the acid remains.

[*E.g.* Heat a little ammonium sulphate or phosphate in a test-tube; ammonia is rapidly evolved, and may be detected by its characteristic smell.]

(*c*) The ammonium salts of certain oxyacids which readily part with oxygen (such as ammonium nitrate, nitrite, chromate) are also decomposed by heat, the ammonia being oxidised to nitrogen or oxides of nitrogen.

[*E.g.* Heat a few crystals of ammonium nitrate in a test-tube. Examine the gas with a taper and a glowing splint of wood.]

$$NH_4NO_3 = 2H_2O + N_2O$$
$$NH_4NO_2 = 2H_2O + N_2$$
$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$$

Ammonium is separated from the other members of the group by evaporating the solution to dryness, and strongly heating the residue until the ammonia is completely expelled, which may generally be regarded as accomplished when fumes are no longer given off.

Wet Reactions.—Ammonium salts are all soluble in water, therefore it is only in concentrated solutions that any precipitations with reagents can be formed. *Use ammonium chloride.*

Caustic alkalies (NaHO or KHO) and oxides or hydroxides of metals of the alkaline earths (*e.g.* CaO, $Ba(HO)_2$), when heated with an ammonium salt, cause the evolution of ammonia gas, NH_3.

$$(NH_4)_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O + 2NH_3$$
$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$$

In practice, sodium hydroxide solution is added either to the solid salt or to its solution in water, and the mixture gently warmed. The evolved ammonia may be recognized (1) by its characteristic odour if present in sufficient quantities; (2) by its power of restoring the blue colour to moist reddened litmus paper, or of turning turmeric paper brown; (3) by the formation of white fumes when a glass rod moistened with strong hydrochloric acid is held in the mouth of the test-tube.

[In special cases, as in the examination of natural waters, minute traces of ammonia are detected by the use of Nessler's solution (a solution of potassium mercuric iodide in potash), which gives either a brown precipitate or a coloration, according to the amount of ammonia present, $2(HgI_2,2KI) + 3KHO + NH_3 = NHg_2''I,H_2O + 7KI + 2H_2O$.]

Platinum chloride, $PtCl_4$, precipitates from *concentrated solutions* a yellow crystalline compound, ammonium chloroplatinate, $(NH_4)_2PtCl_6$ (sometimes called ammonium platinic chloride, $2NH_4Cl$, $PtCl_4$), soluble in 170 parts of water at 10°; insoluble in alcohol and ether. This compound is distinguished from the similar potassium salt in that, when strongly heated, it leaves a residue of spongy platinum only.

Tartaric acid, $H_2(C_4H_4O_6)$, or hydrogen sodium tartrate, $HNa(C_4H_4O_6)$, produces in concentrated solutions a white precipitate of hydrogen ammonium tartrate, $H(NH_4)(C_4H_4O_6)$. Soluble in water, in mineral acids, and in alkalies; insoluble in alcohol. This compound is distinguished from the corresponding potassium salt by the fact that when strongly heated, the carbonaceous residue is without any alkaline reaction.

[When tartaric acid is used, the acid previously in combination with the ammonia is liberated by the double decomposition, thus—

$$NH_4Cl + H_2(C_4H_4O_6) = H(NH_4)(C_4H_4O_6) + HCl$$

And as the precipitate is soluble in mineral acids, the delicacy of the reaction is increased by employing hydrogen sodium tartrate as the reagent, in which case no free acid is formed in the reaction, thus—

$$NH_4Cl + HNa(C_4H_4O_6) = H(NH_4)(C_4H_4O_6) + NaCl]$$

Sodium, Na.

Dry Reaction.—Sodium compounds, when heated upon a platinum wire in a Bunsen flame, undergo volatilisation, and impart to the flame a brilliant golden yellow colour. This flame-reaction is the most characteristic and delicate test for this metal.*

Wet Reactions.—All sodium salts are soluble; sodium platinochloride is soluble in water, in alcohol, and in ether. Hydrogen sodium tartrate also is freely soluble in water. Sodium pyroantimonate,† however, is less soluble in water than the corresponding

* When the light emitted by heating a sodium salt in the Bunsen flame is examined by the spectroscope (see p. 27), it is found to be *monochromatic*, i.e. to consist of one colour only, namely, pure yellow light. Any coloured object whose colour contains *no yellow* in its composition, when illuminated only by the light emitted by the sodium flame, appears black. The red colouring matter in blood, for example, contains no yellow; hence blood, when seen only in the light of the sodium flame, looks *black*: for this reason, the hands and face of a person illuminated only by the sodium flame appear black and dirty in proportion as the individual has a high colour or not. Indigo, and many other common coloured materials, similarly absorb the yellow light emitted by sodium, hence if the sodium flame be viewed through a thin stratum of such a coloured solution, the yellow light is entirely intercepted. For the use that is made of this property, see potassium (p. 22).

† Formerly misnamed sodium *metantimonate*. For a comparison of phosphates, arsenates, and antimonates, see Newth's "Inorganic Chemistry," p. 458.

potassium salt, and is therefore precipitated by the addition of a strong solution of potassium pyroantimonate to a strong solution of a sodium salt, such as sodium chloride, thus—

$$H_2K_2Sb_2O_7 + 2NaCl = H_2Na_2Sb_2O_7 + 2KCl$$

Potassium, K.

DRY REACTION.—When potassium compounds are heated upon a platinum wire in a Bunsen flame, they impart to the flame a pale violet or lilac colour. This delicate tint, however, is completely masked by the intense yellow colour which the presence of even minute quantities of sodium compounds impart to the flame.

Introduce a fragment of potassium nitrate into the Bunsen flame upon a loop of clean platinum wire ;* notice the lilac colour imparted to the flame. Now look at the flame through a *potassioscope*,† and observe that it appears a brilliant crimson-red colour. Upon another wire introduce a particle of sodium chloride into the flame, and notice that when this is examined through the potassioscope, the intense golden yellow light is absolutely cut off, and is invisible. Now touch the wire containing the nitre with a fragment of sodium chloride, and again bring it into the flame. The yellow of the sodium completely overpowers and masks the violet of the potassium when viewed direct, but if looked at through the potassioscope, the red colour due to the potassium shines up as brilliantly as before, while the yellow is completely intercepted ‡ (see also p. 33).

* By merely touching the wire with the fingers, it contracts sufficient sodium compounds to give the yellow flame. To clean it, it should be dipped in hydrochloric acid and heated until it ceases to impart any colour to the flame.

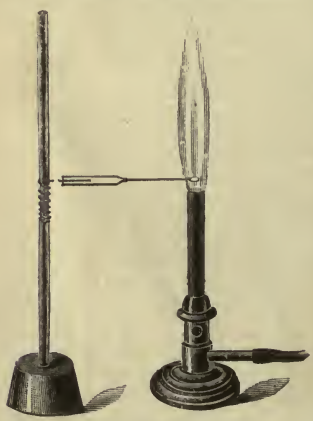

FIG. 8.

† The potassioscope is a little instrument consisting of a flat circular glass cell filled with a solution of one of the rose-aniline blue colouring matters. It possesses the advantage over the older *indigo prism*, in that it not only makes it possible to detect potassium in the presence of sodium (which a solution of indigo does equally well), but, owing to the fact that it entirely intercepts the red light emitted by lithium, barium, strontium, and calcium, it renders it possible to detect potassium with certainty, even when any of these other elements are present.

‡ When studying flame reactions, it is often of the greatest convenience to use a stand on which to support the platinum wire, so that the hands may be free ; a simple stand is readily constructed as shown in Fig. 8. A piece of glass tube or glass rod is inserted in a large cork (rubber, being heavier, makes a steadier foot), and a piece of galvanized iron wire is twisted two or three times round

WET REACTIONS.—Most potassium salts are soluble in water. *Use a solution of potassium chloride.*

Platinum chloride, $PtCl_4$, produces, with concentrated solutions of potassium salts, a yellow crystalline precipitate of potassium chloro-platinate (or *potassium platinic chloride*), K_2PtCl_6, soluble in 110 parts of water at 10° (therefore more soluble than the corresponding ammonium compound). Soluble in alkalies (therefore the solutions used should be acid); nearly insoluble in alcohol; quite insoluble in a mixture of alcohol and ether (therefore the precipitation of this compound is promoted by the addition of alcohol).

Hydrogen sodium tartrate, $HNa(C_4H_4O_6)$, gives, with solutions of potassium salts, a white crystalline precipitate of hydrogen potassium tartrate, $HK(C_4H_4O_6)$; soluble in much water, and also in acids and alkalies (therefore the solution should be both concentrated and neutral). The precipitate is insoluble in alcohol.

Hydrofluosilicic acid (or **silico-fluoric acid**), H_2SiF_6, throws down a white precipitate of gelatinous appearance, consisting of potassium silicofluoride, K_2SiF_6, sparingly soluble in water.

Magnesium, Mg.

In the "natural classification" of the elements, magnesium is associated with the metals of the alkaline earths (Be, Ba, Sr, Ca) on the one hand, and with zinc and cadmium on the other. Its position along with the alkalies in Group V. of the analytical classification, is simply because it differs from the other members of its own natural family in that the presence of ammonium chloride prevents the precipitation of magnesium hydroxide by ammonia in Group III., and also of magnesium carbonate by the group reagent of Group IV.

DRY REACTION.—When magnesium salts are strongly heated in the outer blowpipe, a white infusible residue of the oxide is left. If, after cooling, the residue be moistened with a drop or two of cobalt nitrate solution and again strongly heated in the outer blowpipe flame, the mass acquires a pink colour. This reaction is reliable only in the absence of other metallic oxides.

WET REACTIONS.—Of the common salts of magnesium, the sulphate, chromate, nitrate, and halogen salts are soluble in water. One prominent characteristic of magnesium compounds is the

the rod with one end projecting at right angles to the upright. The little glass tube into which the platinum wire is fused, is then slipped over the projecting iron wire. This arrangement admits of the wire being raised or lowered as desired, while at the same time it readily remains in any position.

readiness with which they form "double" salts, many of which are soluble in water. *Use magnesium sulphate.*

Alkaline hydroxides (NH_4HO, KHO, NaHO, $Ca(HO)_2$, or $Ba(HO)_2$) precipitate from solutions of magnesium sulphate or chloride, white magnesium hydroxide, $Mg(HO)_2$. Almost insoluble in water; soluble in acids, soluble in ammonium chloride—

$$Mg(HO)_2 + 4NH_4Cl = 2NH_4HO + MgCl_2,2NH_4Cl \text{ (soluble double salt)}$$

Owing to the solubility of magnesium hydroxide in ammonium chloride, only half the magnesium is precipitated from magnesium chloride by means of ammonia, thus—

$$2MgCl_2 + 2NH_4HO = Mg(HO)_2 + MgCl_2,2NH_4Cl$$

If ammonium chloride is previously present in sufficient quantity to combine with the whole of the magnesium hydroxide, the alkaline hydroxides give no precipitate.

Alkaline carbonates (K_2CO_3, Na_2CO_3, $(NH_4)_2CO_3$) produce in solutions of magnesium salts, in the absence of ammonium salts, precipitates of basic carbonates of magnesium, the composition of which varies with conditions of temperature and concentration. The precipitate with $(NH_4)_2CO_3$ only separates out after a short time. *In the presence of ammonium chloride these reagents give no precipitate.*

Hydrogen disodium phosphate, HNa_2PO_4, precipitates hydrogen magnesium phosphate, $HMgPO_4$, and tri-magnesium phosphate, $Mg_3(PO_4)_2$. In the presence of ammonium chloride, however, the double ammonium magnesium phosphate is thrown down as a white crystalline precipitate, NH_4MgPO_4. It is appreciably soluble in water, but *insoluble in ammonia;* hence ammonia must be previously added.

In very dilute solutions the precipitation only takes place on long standing. It is accelerated by stirring with a glass rod, the deposition first appearing where the rod has rubbed the glass vessel. The precipitate is soluble in acids, even acetic acid, but reprecipitated by ammonia.

Systematic Plan of Analysis for the Metals of Group V.

After having carefully gone through the various reactions for the metals of Group V., the student should proceed to the examination of a few solutions containing mixtures of two or more salts of these metals.

The various special tests by which the individual members of this group are recognised are not, for the most part, interfered with by the presence of the rest of the group. Therefore a complete separation of all the metals is not necessary. Thus, the test for ammonium (evolution of ammonia by heating with sodium hydroxide) can be made in the presence of Mg, K, and Na compounds; and obviously *must* be made in a separate portion of the solution under examination from that in which sodium is to be tested for, as it involves the *addition of a sodium compound.*

The test for magnesium, likewise (precipitation of NH_4MgPO_4), may be made in the presence of all the other members; and clearly must be made also in a separate portion of the solution, as it involves the addition of both ammonium and sodium compounds. Similarly, the flame tests for potassium and sodium are not interfered with by the presence of ammonium or magnesium. The flame reaction for potassium, however, unless examined by the aid of the potassioscope, must always be corroborated by the formation of potassium chloroplatinate. But before this test can be applied, ammonium salts must first be removed.

Solutions may be examined for the metals of Group V., NH_4, Na, K, Mg, by the following system :—

Detection of the Metals of Group V.

Operation 1.—To a portion of the solution add NaHO, and heat in a test-tube. The evolution of ammonia (detected by its odour, and its action on test-papers) proves the presence of NH_4.

Operation 2.—To a second portion add NH_4Cl, NH_4HO, and HNa_2PO_4. A white crystalline precipitate of NH_4MgPO_4 proves the presence of Mg.

Operation 3.—Evaporate another (and larger) portion to dryness in a porcelain dish. If ammonium salts are present * (already ascertained in Operation 1), they must be removed. For this purpose, scrape the residue out of the dish and strongly heat it on the lid of a platinum crucible (or a piece of platinum foil), until, on momentarily withdrawing it from the flame, fumes are no longer visible.

Dissolve the residue in a *small quantity* of water, and add one drop of HCl. Dip a *clean* platinum loop into the solution, and heat

* In a *complete* analysis, ammonium salts are always present here, as they will have been introduced in the process of separating the other groups. Under these circumstances, therefore, the operation of removing ammonium compounds is always necessary. The substance under analysis is tested for ammonium *before* the ammoniacal reagents are introduced.

it in a Bunsen flame. An *intense** yellow coloration proves the presence of Na. A lilac colour indicates the presence of K.

In either case examine the flame through the potassioscope; a crimson flame indicates K.

Add to the solution of the residue a few drops of $PtCl_4$, and stir with a glass rod. A yellow precipitate of K_2PtCl_6 confirms K.

APPENDIX TO CHAPTER III.

LITHIUM, RUBIDIUM, AND CÆSIUM.

These three elements are usually placed in the category of *rare metals*. It must be remembered, however, that there are *degrees* of rarity; and while the compounds of rubidium and cæsium are certainly among the very rare substances with which the chemist comes into contact, those of lithium, on the other hand, are very widely distributed and are much more frequently met with.†

Lithium, Li.

DRY REACTION.—Lithium salts impart to the flame a brilliant carmine-red colour.

WET REACTIONS.—All the common salts are readily soluble in water, except the carbonate, phosphate, and oxide, which are soluble with difficulty. The chloride and nitrate are soluble in a mixture of alcohol and ether (*distinction from Na and K, the chlorides and nitrates of which are not soluble*).

Na_2CO_3 and K_2CO_3 precipitate Li_2CO_3 from cold moderately concentrated solutions (1 part dissolves in 100 parts of water).

HNa_2PO_4 gives a white precipitate, on boiling, of Li_3PO_4. The precipitation is complete in the presence of NaHO.

$PtCl_4$ gives no precipitate (*distinction from* NH_4, K, Rb, Cs).

$HNa(C_4H_4O_6)$, hydrogen sodium tartrate, gives no precipitate.

Rubidium, Rb, and Cæsium, Cs.

The compounds of these metals present the very closest resemblance to those of potassium, and there are scarcely any

* More or less of a yellow flame is usually obtained, owing to the presence of traces of sodium compounds as impurities in the reagents previously used in separating the groups in the course of a complete analysis.

† Perhaps a rough idea of the relative rarity of the compounds of these metals might be gained by a comparison of their cost. Lithium salts can be obtained for about 12*s.* per pound, while rubidium and cæsium salts cost about 5*s.* per drachm, *i.e.* at the rate of £64 per pound.

chemical reactions by which they can be distinguished. The separation of these metals is based on the different degrees of solubility of their chloro-platinates. In this respect, as well as in their other properties,* rubidium stands intermediate between potassium and cæsium.

When heated in a Bunsen flame, rubidium and cæsium salts impart to it a lilac colour, which to the unaided eye is absolutely indistinguishable from that produced by potassium compounds; and when compounds of these metals, as well as those of lithium, are mixed with comparatively minute quantities of sodium salts, the colours they give to the flame are completely overpowered and masked by the yellow of the sodium. By means of the spectroscope, however, not only are the apparently identical colours given by potassium, rubidium, and cæsium proved to consist of light of different quality or composition, but the presence of any or all of them is easily and certainly detected even when admixed with sodium salts.

The spectroscope is an instrument by means of which the light emitted by strongly heated substances can be examined after it has been made to pass through a glass prism. Its use depends upon the fact that different coloured lights possess different degrees of refrangibility; that is to say, different coloured rays of light are bent out of their straight course, by passage through a prism, at different angles. Ordinary white light is composed of rays of all degrees of refrangibility, hence, when such light passes through a prism, the various coloured rays are separated, and spread out in the order of their refrangibility, the least refrangible red at one extreme, to the deep violet at the other. This familiar "rainbow" coloured band of light is called the *continuous spectrum.*

In the spectroscope the light is passed through a narrow slit at one end of a small telescope, and an image of the slit is received upon a glass prism. This bends the light out of its straight course, and spreads it out into the various colours of which it is composed. If white light be admitted, then the continuous spectrum is seen, which is an infinite number of images of the slit arranged side by side; if such a *mono*chromatic light as that given by heating sodium salts in the flame be used, then *one* image of the slit is seen in that part of the spectrum which corresponds to the particular degree of refrangibility of the light. In this case we say that the spectrum of sodium consists of one *line* (that is, one image of the slit) in the *yellow*, or *one yellow line.*† The light which passes out of the prism is usually examined by a second telescope, which can be revolved round the prism so that it can sweep the whole length of the spectrum.

When the red colour imparted to the Bunsen flame by a

* Atomic weights, melting-points, etc. Also in the optical properties of their crystallized salts (Tutton, J. C. S., May, 1896).

† When this sodium line is examined by a higher dispersive power, it is found to consist of a group of lines.

lithium salt is examined by the prism, it is seen to consist of light of two degrees of refrangibility, therefore two images of the slit are seen, one in the bright orange (a little on the red side of the sodium line), and the other an extremely brilliant image in the red. The spectrum of lithium, therefore, is one bright orange line and one brilliant red line (see Fig. 9).

Similarly, when the lilac flame of potassium is examined in this way, the light is found to be composed of three colours ; therefore

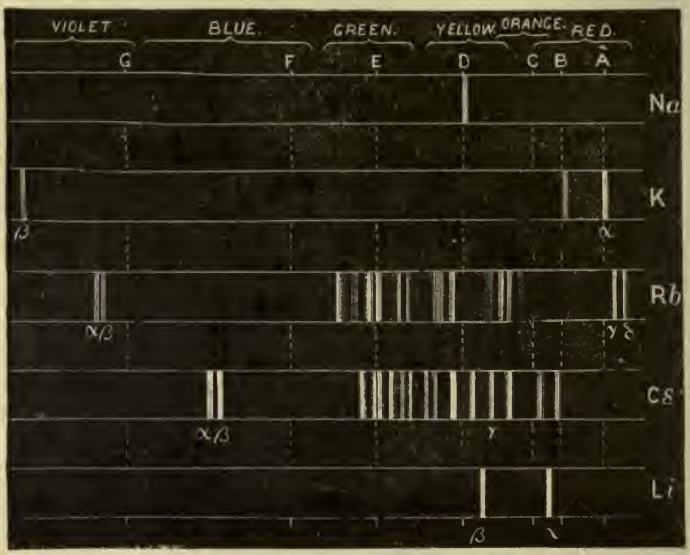

Fig. 9.

three lines are seen—one extremely bright line far down in the red ; a second, less brilliant, about halfway between the first and the yellow sodium (or D) line ; while the third is far away in the deep violet, and not easy to see.*

If a mixture of salts of sodium, potassium, and lithium be heated in a flame, and the light examined by the spectroscope,† then all

* The sodium D line will be also visible, not only on account of the presence of traces of sodium compounds in the other salts, but owing also to the presence of particles of salt which are always floating about in the air, and which tinge the Bunsen flame.

† Where the equipment of the laboratory will allow, every student should have the opportunity of examining the spectra of the metals of the alkalies and alkaline earths.

six lines are seen ; sodium, *one yellow ;* potassium, *two red and one violet ;* lithium, *one red and one orange.*

In such a simple mixture as this there is no difficulty in identifying the various lines of the different elements, but in more complex spectra it is only possible to do so by recording the exact position they each occupy on some fixed scale.

When the spectra of rubidium and cæsium are in this way compared with that of potassium, a striking difference is at once observed. In the first place, they are obviously much more complex. Rubidium shows two strongly marked red lines (hence the name of the element) very close together, and near to the red line of potassium. Then a number of lines in the orange-red and in the green, and lastly two characteristic and brilliant violet lines.

Cæsium gives red lines (not so far down as those of rubidium) orange and green lines, and two most characteristic brilliant lines in the bright blue part of the spectrum (*cæsium* signifies *sky-blue*).

In the chart (Fig. 9), the most prominent lines * in the spectra of the five metals of the alkalies are compared together. The letters at the top refer to lines in the solar spectrum mapped by Fraunhofer, which correspond to those given by known metals. Thus, the D line in the solar spectrum corresponds to the yellow line of sodium.

* Speaking generally, it may be said that at higher temperatures than can be obtained in the Bunsen flame, lines will appear in the spectrum of a particular metal which are not seen at the lower temperature.

CHAPTER IV.

Reactions of the Metals of Group IV.

This group consists of the three metals, **barium, strontium,** and **calcium,** known as the metals of the *alkaline earths.*

The group-reagent, ammonium carbonate, precipitates the carbonates of the metals in an ammoniacal solution, even in the presence of ammonium chloride. Hence the group-reagent separates these three metals from magnesium.

Barium, Ba.

Dry Reaction.—Barium compounds, heated on platinum wire in the Bunsen flame, impart a pale apple-green colour to the flame, which becomes more distinct if the substance on the wire is moistened with strong hydrochloric acid. The test is not very reliable.

Barium sulphate, $BaSO_4$ (also $SrSO_4$ and $CaSO_4$), when heated on charcoal or with carbon, is reduced to the sulphide.

Wet Reactions.—Of the common salts of barium, the chloride, bromide, iodide, nitrate, chlorate, acetate, and sulphide are soluble in water.

Ammonium carbonate, $(NH_4)_2CO_3$, group-reagent (also Na_2CO_3 and K_2CO_3) precipitates barium carbonate, $BaCO_3$, as a white amorphous powder. Insoluble in water; readily dissolved, with evolution of carbon dioxide, by dilute acids; *slightly soluble* in NH_4Cl.

It is also dissolved by a solution of carbon dioxide in water, forming hydrogen barium carbonate, $H_2Ba(CO_3)_2$.*

* On this account complete precipitation of barium carbonate cannot be accomplished by hydrogen ammonium carbonate, HNH_4CO_3, for carbon dioxide is evolved, which dissolves a portion of the precipitate—

$$2HNH_4CO_3 + BaCl_2 = BaCO_3 + 2NH_4Cl + H_2O + CO_2$$

And since the solution of ammonium carbonate used as the group-reagent consists chiefly of HNH_4CO_3 (because the normal salt undergoes decomposition into the hydrogen salt and free ammonia when in aqueous solution), it is always necessary to first add NH_4HO before applying the group-reagent.

H_2SO_4, or any soluble sulphate, produces a white granular precipitate of $BaSO_4$, practically insoluble in water, insoluble also in acids and alkalies. (Boiling concentrated H_2SO_4 slowly dissolves it, forming hydrogen barium sulphate, $H_2Ba(SO_4)_2$.) Insoluble in solutions of $(NH_4)_2SO_4$. $BaSO_4$, being practically insoluble in water, is precipitated by a saturated solution of $SrSO_4$, although such a solution contains only 1 part of salt in 7000 parts of water.

Potassium chromate, K_2CrO_4, produces a primrose-yellow precipitate of barium chromate, $BaCrO_4$, practically insoluble in water (*distinction from* $SrCrO_4$, *which is* MODERATELY *soluble, ana* $CaCrO_4$, *which is* VERY *soluble in water*). It is insoluble in acetic acid (distinction from $SrCrO_4$); soluble in HNO_3 and in HCl. By boiling with K_2CO_3, barium chromate is converted into the carbonate—

$$BaCrO_4 + K_2CO_3 = BaCO_3 + K_2CrO_4$$

Hydrofluo silicic acid, H_2SiF_6, gives a white crystalline precipitate of barium silicofluoride, $BaSiF_6$, slightly soluble in water, but insoluble on the addition of alcohol (distinction from $SrSiF_6$ and $CaSiF_6$, which are readily soluble in water).

Strontium, Sr.

DRY REACTION.—When heated in the Bunsen flame, volatile strontium salts, such as $SrCl_2$, $Sr(NO_3)_2$, impart a rich crimson colour to the flame; other salts require to be moistened upon the wire with strong HCl. Strontium sulphate must be converted into the sulphide, which is then dissolved in HCl and the chloride tested in the flame.*

WET REACTIONS.—The same common salts of strontium as of barium are soluble in water. The chromate and sulphate are somewhat soluble.

$(NH_4)_2CO_3$ (Na_2CO_3 and K_2CO_3) precipitates $SrCO_3$, exactly similar to the barium compound in its reactions.

H_2SO_4 or soluble sulphates precipitate $SrSO_4$. The precipitate is slightly soluble in water (1 : 7000), considerably soluble in HCl or HNO_3, but almost insoluble in a solution of $(NH_4)_2SO_4$ (*distinction from* $CaSO_4$). $SrSO_4$ is precipitated by a solution of

* Small quantities of $SrSO_4$ upon a filter may be converted into SrS by first drying the filter, then folding it into a small roll, and twisting a platinum wire round it so as to hold it in a flame. The paper is burnt to an ash, and the latter is then heated upon the wire in an ordinary smoky gas-flame, when the reduction of the sulphate takes place. The ash is then touched with a glass rod dipped in strong HCl, and on bringing it into a Bunsen flame the crimson flame is seen.

$CaSO_4$* (a saturated solution of which only contains 1 part in 430 parts of water); the precipitation does not take place *at once* in cold solutions, but appears quickly on heating.

K_2CrO_4 and **H_2SiF_6** (see barium reactions with these reagents)

Calcium, Ca.

DRY REACTIONS.—Calcium compounds, when heated in a Bunsen flame, impart to it a reddish colour, especially if previously moistened with hydrochloric acid. The presence of strontium masks the red colour given by calcium compounds. When calcium carbonate is strongly heated it loses carbon dioxide, and is converted into calcium oxide—

$$CaCO_3 = CO_2 + CaO$$

This process is carried on in the lime-kilns during the operation of "burning lime." Limestone (*calcium carbonate*) is thus converted into lime (*calcium oxide*). $SrCO_3$ and $BaCO_3$ undergo similar decomposition; $SrCO_3$ less readily than $CaCO_3$, while $BaCO_3$ requires prolonged heating to a white heat to effect the change.

WET REACTIONS.—The same common salts of calcium are soluble in water as of strontium and barium; and, generally speaking, calcium salts are more *readily* soluble. Thus, the chloride and nitrate are extremely deliquescent; the sulphate dissolves to the extent of 1 : 430 (compare Sr and Ba). The solubility of the oxalates, however, is in the reverse order, calcium oxalate being the most insoluble, and barium oxalate the most soluble. A peculiarity of calcium salts is that many of them appear to be *less soluble in hot than in cold water.*

$(NH_4)_2CO_3$ (also Na_2CO_3 and K_2CO_3) precipitates $CaCO_3$, similar to the barium and strontium compounds in its reactions.

H_2SO_4 or soluble sulphates,† added to a *strong* solution of a calcium salt,‡ give an *immediate* precipitate of calcium sulphate.

* $SrSO_4$ is itself soluble in water to the extent of 1 : 7000, but obviously the addition of a solution of $CaSO_4$ or H_2SO_4 to this solution does not precipitate the $SrSO_4$. Neither is the strontium precipitated from this solution by any reagent which forms with it a compound which is more soluble in water than is the sulphate, *e.g.* oxalic acid or oxalates.

† The soluble sulphate must be *more* soluble than calcium sulphate; $SrSO_4$ therefore, being *less* soluble, would not give a precipitate with a solution of a calcium salt, although, being *more* soluble than $BaSO_4$, it throws down this compound from solutions of barium salts. For the same reason, a solution of $CaSO_4$ will throw down $SrSO_4$ and $BaSO_4$ from solutions of strontium and barium salts.

‡ Only in the case of calcium salts which are *more* soluble than calcium sulphate.

From more dilute solutions the precipitate only separates after some time, or, if still more dilute, not at all. The precipitate is insoluble in alcohol, therefore the addition of this liquid in considerable bulk favours the precipitation.

Calcium sulphate is readily soluble in a concentrated solution of ammonium sulphate, especially when hot (*distinction from* $SrSO_4$ *and* $BaSO_4$). Boiling with potassium carbonate easily converts it into calcium carbonate.

Oxalic acid, $H_2C_2O_4$, or soluble oxalates, gives a white crystalline precipitate of calcium oxalate. The precipitate is soluble in mineral acids; hence, when oxalic acid is used as the precipitant, precipitation is not complete, owing to the liberation of the mineral acid of the calcium salts, thus—

$$CaCl_2 + H_2C_2O_4 = CaC_2O_4 + 2HCl$$

Calcium oxalate is insoluble in NH_4HO, therefore, if the solution be first rendered alkaline, the whole of the oxalate is thrown down. In practice it is usual to employ ammonium oxalate, $(NH_4)_2C_2O_4$. In cold dilute solutions precipitation is not immediate. The precipitate is insoluble in water and in acetic acid. Strontium and barium oxalates are soluble, to a small extent, both in water and in acetic acid.

Spectra of Barium, Strontium, and Calcium.

The spectra given by these metals, when their salts are heated in the Bunsen flame, are extremely characteristic. For calcium, the chloride may be used, with occasional moistening with hydrochloric acid. For barium and strontium, the nitrates, or, better still, the chlorates give the best result, although in the absence of these salts the chlorides can be employed.

From the charts of their spectra given in Fig. 10, it will be seen that they each give lines in the red portion of the spectrum. Owing to this fact, if salts of these metals are heated in a Bunsen flame, and the flame examined through an *indigo prism*, the flame will appear *red* in each case, because indigo does not intercept or absorb the red portion of the spectrum. The potassioscope, on the other hand, has the property of cutting off the red rays emitted by these metals. It absorbs all the red part of the spectrum down very nearly to the prominent red line (K.α) of potassium (compare the chart on p. 28), beyond the lithium and cæsium red lines. Hence, if flames which are coloured by the alkaline earths are examined through this instrument, *no red* will be visible.

The importance of this lies in the following fact: When Groups IV. and V. are separated by precipitating the carbonates of barium, strontium, and calcium, minute traces of these metals pass through into Group V., as their carbonates are not *absolutely* insoluble. Hence, when the final residue is obtained (in which the tests for

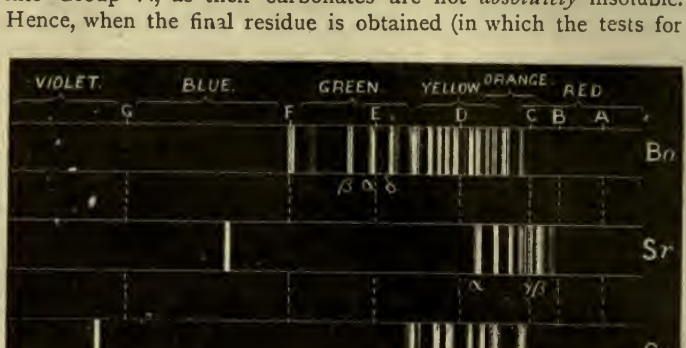

FIG. 10.

potassium are made), it will contain these traces of these alkaline earths. If this residue be tested in the flame, and the flame examined by the potassioscope, the presence of these members of Group IV. will not vitiate the reaction; but with the indigo prism the red light they emit would be mistaken for, and returned as that given by potassium.*

SEPARATION OF GROUPS IV. AND V.

The solution is first rendered alkaline by the addition of NH_4HO. NH_4Cl is then added (to prevent the precipitation of magnesium carbonate), after which ammonium carbonate is added until the carbonates of the metals of Group IV. are completely thrown down. The mixture may be gently warmed. [It must not be boiled, or the precipitated carbonates will react with the NH_4Cl, forming soluble chlorides, while NH_3 and CO_2 will escape with the steam; thus, $BaCO_3 + 2NH_4Cl = BaCl_2 + CO_2 + 2NH_3 + H_2O$.] The mixture is filtered. The filtrate is examined for the metals of Group V. by the method given on p. 25, while the precipitate is treated in the following way:—

* The only element which could be mistaken for potassium, when using the potassioscope, is the exceedingly rare metal rubidium, whose spectrum contains red lines still lower down than those of potassium.

Separation of the Metals of Group IV.

The **precipitate**, consisting of $BaCO_3$, $SrCO_3$, and $CaCO_3$, is washed, and then dissolved in a small quantity of warm dilute acetic acid, $H(C_2H_3O_2)$. To the solution thus obtained potassium chromate, K_2CrO_4, is added; the mixture gently warmed and filtered.*

The **precipitate** consists of yellow barium chromate, $BaCrO_4$.

Boil the precipitate with K_2CO_3, which converts $BaCrO_4$ into $BaCO_3$. Filter, and wash the precipitate free from the K_2CrO_4. Dissolve the precipitate in HCl, and confirm by $SrSO_4$ or H_2SiF_6.

The **filtrate**† contains strontium and calcium acetates. Add a strong solution of $(NH_4)_2SO_4$, and boil for a short time to ensure the solution of $CaSO_4$. Filter.

The **precipitate** consists of $SrSO_4$.

Wash the precipitate thoroughly, and confirm by the flame reaction.

The **solution** contains calcium sulphate. Add ammonium oxalate, $(NH_4)_2C_2O_4$ (or $(NH_4)HO$ and oxalic acid, $H_2C_2O_4$). A white precipitate of CaC_2O_4 confirms calcium.

Other methods of separating the metals of Group IV., based on the insolubility of certain of their common salts in alcohol, may be employed. Thus, the nitrates of barium and of strontium are insoluble in alcohol, while that of calcium is soluble in this liquid (or mixtures of alcohol and ether).

The precipitated carbonates are dissolved in dilute HNO_3, and the solution evaporated to dryness. The residue, consisting of the mixed nitrates, is then treated with a mixture of alcohol and ether, in about equal volumes, which dissolves the $Ca(NO_3)_2$, leaving $Ba(NO_3)_2$ and $Sr(NO_3)_2$.

Again, barium chloride is insoluble in the same mixture, whereas the chlorides of strontium and calcium are both soluble. Therefore, if the mixed carbonates are dissolved in dilute HCl, and the solution evaporated to dryness, the $SrCl_2$ and $CaCl_2$ may be dissolved out, leaving a residue of $BaCl_2$.

* Instead of adding the chromate at once to the whole of the solution, a small separate portion may be used, and the presence or absence of the Ba thus ascertained. If *present*, then the whole of the solution is treated as above, and the precipitation of barium chromate may then be taken as confirmatory. If *absent*, then a second small portion of the solution is taken, and tested for Sr by adding $CaSO_4$. If Sr is present, then the separation of Sr and Ca is carried out as shown above; but if $CaSO_4$ gives no precipitate even on warming, thus proving the absence of Sr, the remainder of the solution is at once tested for Ca by the oxalate reaction.

† If barium has been separated as chromate, the filtrate will be coloured yellow by the excess of K_2CrO_4 used, and a *white* precipitate may appear yellow. The process is more thorough if the carbonates of Sr and Ca are again thrown down by adding ammonium carbonate. The precipitate is then washed free from chromate, dissolved in a few drops of HCl, and the sulphates separated as directed above.

CHAPTER V.

The Metals of Group III.

This group comprises the metals **aluminium, chromium, iron, manganese, zinc, nickel,** and **cobalt,** besides a number of the rare metals (see Classification, p. 16).

Although all these metals are precipitated by the group-reagent, namely, **ammonium sulphide,** in the presence of ammonia, the compounds that are thrown down are not all of similar composition, as was the case in Group IV.

The addition of ammonia to a solution containing the metals of this group, results in the precipitation of the hydroxides (or hydrated oxides) of Al, Cr, and Fe, corresponding to the oxides R_2O_3.* Thus, taking aluminium in potash alum as an example—

$$K_2SO_4,Al_2(SO_4)_3 + 6NH_4HO = K_2SO_4 + 3(NH_4)_2SO_4 + Al_2(HO)_6$$

In the presence of ammonium chloride, the hydroxides of the metals Mn,† Zn, Ni, and Co (which have the general formula $R(HO)_2$) are not precipitated by ammonia, owing to the formation of double chlorides.

If ammonium sulphide be added to the mixture after the ammonia, the already precipitated hydroxides of aluminium and chromium are unchanged, but the ferric hydroxide is converted into *ferrous* sulphide, with the elimination of sulphur; thus—

$$Fe_2(HO)_6 + 3H_2S = 2FeS + 6H_2O + S$$

and the remaining metals are also thrown down as sulphides.

* The separation of the metals of Group III. is complicated by the fact that if Mn, Zn, Ni, and Co are present in the form of *phosphates,* the addition of ammonia causes the partial precipitation of these phosphates. And, further, if the members of Group IV. and Mg are present as phosphates, they also are thrown down by ammonia, and therefore appear in Group III. The special treatment of phosphates will be discussed later.

† In the case of manganese, the separation is not complete under all conditions (see reactions of manganese).

The result, therefore, of adding NH_4Cl, NH_4HO, and $(NH_4)_2S$ is as follows :—

Precipitated by NH_4HO in the presence of NH_4Cl	$Al_2(HO)_6$, $Cr_2(HO)_6$, $Fe_2(HO)_6$	converted into FeS	*
——		MnS	Precipitated on the addition of $(NH_4)_2S$
——		ZnS	
——		NiS	
——		CoS	

The metals of Group III., therefore, may be subdivided into two families, based upon their behaviour towards ammonia : Division A, consisting of the three metals, aluminium, chromium, and iron ; and Division B, of manganese, zinc, nickel, and cobalt.

REACTIONS OF THE METALS OF GROUP III.—DIVISION A.

Aluminium, Al.

DRY REACTION.—When aluminium compounds are strongly heated on charcoal in the outer flame, aluminium oxide is formed, and if this be moistened with a solution of cobalt nitrate, and again strongly heated, either upon the charcoal or upon a loop of platinum wire, the mass assumes a rich blue colour, due to the formation of cobalt aluminate.

This test is, however, greatly masked if other metallic oxides which are coloured are present at the same time. It may be employed as a confirmatory test when aluminium is separated from iron and chromium in the course of analysis.

WET REACTIONS.—Of the common salts of aluminium, the chloride, Al_2Cl_6, and sulphate, $Al_2(SO_4)_3$, are soluble in water. The important salts, however, are the double sulphates of aluminium with ammonium or potassium, known as *ammonium alum*, $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$, and *potassium alum*, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, respectively.† A solution of either of these alums may be used for the following reactions.

* In reality the compounds precipitated are the hydrated sulphides, expressed by the general formula R(HS)(HO), or RS,H_2O. To avoid unnecessary complication in reactions, the molecule of H_2O may be left out of consideration.

† The alums constitute a large class of double sulphates, having the general formula $M_2SO_4,R_2(SO_4)_3,24H_2O$, where M is a monovalent element or group, such as potassium or ammonium, and R is either aluminium, iron, chromium, or manganese. The commonest of all the salts is potassium aluminium alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$; this is the salt, therefore, that is distinguished by the single word ALUM. From their formulæ it may be seen at a glance that

NH_4HO throws down a white translucent precipitate of the hydrated oxide, or hydroxide,* $Al_2O_3,3H_2O$, or $Al_2(HO)_6$. Soluble in a large excess of the reagent, but on gently boiling, the hydroxide is entirely precipitated. [Prolonged boiling, however, causes partial dissociation of the ammonium salt in solution, ammonia escapes, and free acid is liberated, which then begins to dissolve the precipitate.] In the presence of ammonium chloride, the precipitation of $Al_2(HO)_6$ by ammonia is complete. The precipitate is readily soluble in mineral acids, and in acetic acid.

KHO or **NaHO** produces the same precipitate, which readily combines with an excess of the reagent, forming a soluble aluminate of potassium or sodium ($Al_2O_3,3Na_2O$ or $Na_6Al_2O_6$). These aluminates are decomposed by acids, even by such feeble acids as carbonic acid or hydrosulphuric acid (sulphuretted hydrogen), with reprecipitation of the aluminium hydroxide, as this compound is not soluble in sodium carbonate or sodium sulphide. Thus, with carbonic acid—

$$Al_2O_3,3Na_2O + 3CO_2 + 3H_2O = 3Na_2CO_3 + Al_2O_3,3H_2O\,[\text{or } Al_2(HO)_6]$$

In the case of stronger acids, such as HCl, the same action takes place, but any excess of the acid beyond that required to combine with the sodium of the aluminate at once re-dissolves the $Al_2(HO)_6$. When, therefore, this acid is used, a slight excess is added, and the aluminium hydroxide is re-precipitated by means of ammonia.

Sodium and potassium aluminates are also decomposed by ammonium chloride, with the precipitation of aluminium hydroxide; the precipitation is complete on boiling. The compound thrown down under these circumstances consists mainly of the di-hydrated oxide, $Al_2O_3,2H_2O$; thus—

$$Al_2O_3,3Na_2O + 6NH_4Cl = 6NaCl + 6NH_3 + H_2O + Al_2O_3,2H_2O$$

these salts are composed of a molecule of each of the two sulphates, together with twenty-four molecules of water. With compounds of this description there is, unfortunately, a tendency in certain quarters to add the formulæ of the two salts together, and then to divide the numerals by their greatest common measure; thus, $K_2SO_4,Al_2(SO_4)_3,24H_2O = K_2Al_2(SO_4)_4,24H_2O$, which, divided by $2 = KAl(SO_4)_2,12H_2O$. Presumably this plan is adopted with a view to simplification, but as it obscures the origin and the nature of the compounds, and as there is not the smallest evidence that such formulæ are more exact representations of the molecular constitution of the compounds, their use is greatly to be deprecated.

* Three hydrated oxides of aluminium are known, obtainable by precipitation under different circumstances, namely, $Al_2O_3,3H_2O$, $Al_2O_3,2H_2O$, and Al_2O_3,H_2O; these may also be formulated $Al_2(HO)_6$, $Al_2O(HO)_4$, and $Al_2O_2(HO)_2$ respectively.

$BaCO_3$ suspended in water, precipitates $Al_2(HO)_6$, carbon dioxide being evolved. The precipitation is complete even in the cold.* If alum or aluminium sulphate is used, the precipitate is mixed with insoluble barium sulphate—

$$Al_2(SO_4)_3 + 3BaCO_3 + 3H_2O = Al_2(HO)_6 + 3BaSO_4 + 3CO_2\dagger$$

K_2CO_3 and **Na_2CO_3** precipitate an uncertain mixture of the hydroxide and basic carbonates.

$(NH_4)_2S$ precipitates aluminium hydroxide, with evolution of sulphuretted hydrogen (compare Fe).—

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(HO)_6 + 3(NH_4)_2SO_4 + 3H_2S\dagger$$

[Aluminium forms no sulphide in the wet way. Al_2S_3 (obtained by the union of Al and S) is decomposed instantly by water, forming the trioxide, and evolving H_2S.]

Chromium, Cr.

DRY REACTIONS.—Chromium compounds impart to a borax bead a grass-green colour, when heated either in the outer or inner blowpipe flame.

When fused in a platinum capsule with five or six times their weight of a mixture consisting of 1 part of KNO_3 and 2 parts of dry Na_2CO_3 or K_2CO_3 (or 1 part of $KClO_3$ with 6 parts of Na_2CO_3), chromium compounds are converted into alkaline chromates, which appear as *a yellow mass, soluble in water to a yellow solution.* In the case of chromic oxide, for instance, Cr_2O_3, the reaction is the following :—

$$Cr_2O_3 + 2K_2CO_3 + KClO_3 = 2K_2CrO_4 + KCl + 2CO_2$$

The chief natural source of chromium is the mineral *chrome iron ore*, Cr_2O_3,FeO. When this is fused with either of the above mixtures, the same reaction takes place as regards the chromium, while the iron is changed to Fe_2O_3 ; thus—

$$6Cr_2O_3,FeO + 12K_2CO_3 + 7KClO_3 = 12K_2CrO_4 + 3Fe_2O_3 + 7KCl + 12CO_2$$

* In the presence of certain organic acids, as oxalic, tartaric, or citric acids, aluminium hydroxide is only more or less imperfectly precipitated by the above-mentioned reagents, owing to the formation of soluble double salts of the organic acid with aluminium and the alkali metal ; such, for example, as the double tartrate of aluminium and sodium, $Na_2(C_4H_4O_6),Al_2(C_4H_4O_6)_3$. This applies also in the case of the corresponding chromium and iron compounds.

† In these equations simple aluminium sulphate is given instead of alum, in order not to unnecessarily load the equation with materials taking no part in the reaction.

[Sodium peroxide, Na_2O_2, may be substituted as the oxidizing material, in which case the fusion should be carried out in a silver capsule.]

WET REACTIONS.—The two best-known classes of chromium salts are derived from the two oxides, namely—

Chromium sesquioxide (or chromic oxide), Cr_2O_3

Chromium trioxide (chromic anhydride), CrO_3

Chromic oxide, Cr_2O_3, is basic, uniting with acids to form the *chromic salts*, such as chromic hydroxide, $Cr_2(HO)_6$ or $Cr_2O_3,3H_2O$; chromic chloride, $CrCl_3$; chromic sulphate, $Cr_2(SO_4)_3$; double potassium and chromium sulphate (*chrome alum*), $K_2SO_4,Cr_2(SO_4)_3$, $24H_2O$. Of these salts, the hydroxide alone is insoluble in water.

Chromium trioxide, CrO_3, is the anhydride of the hypothetical chromic acid,* H_2CrO_4, which gives rise to salts known as *chromates*, analogous in constitution to the sulphates.

Chromates of the metals of Groups IV. and V. are all soluble in water, except $BaCrO_4$. The other chromates are insoluble.

a. **Chromic Salts.**—These salts are mostly of a purplish or violet-grey colour when solid, giving either a purple or green solution when dissolved, the colour depending upon the conditions of solution. Thus chrome alum dissolved in cold water gives a purple solution, which on boiling turns green,† and on long standing again becomes purple.

NH_4HO produces a bluish or greenish-grey precipitate of chromic hydroxide, $Cr_2(HO)_6$‡, partially dissolved by excess of ammonia in the cold, giving a lilac-coloured liquid, but completely precipitated on gently boiling. $Cr_2(HO)_6$ is readily soluble in acids.§

KHO and **NaHO** precipitate $Cr_2(HO)_6$, readily soluble in excess, giving a deep green solution.‖ Reprecipitated by neutralization with HCl, and by boiling with NH_4Cl, as in the case of Al.

* At first it may confuse students to find that chrom*ic* anhydride, and chrom*ic* acid with its salts, should not be in the class of *chromic* compounds. It must be remembered that the *classification* is not based upon the *nomenclature* of the substances. "Chromic" compounds are those containing chromium as the "base," or the positive radical; while in those compounds derived from CrO_3 the element is in the "acidic" or negative group. They may, therefore, be conveniently distinguished as "chromic acid" compounds.

† The green colour is said to be due to the formation of a basic salt, by the action of water upon the normal compound.

‡ The composition of the precipitate depends on the conditions under which it is formed. There are several hydrated chromic oxides; compare also Al.

§ For the influence exerted by the presence of organic acids, see footnote, p. 39.

‖ The soluble compounds produced are similar to those given by aluminium; the potassium salt has the composition Cr_2O_3,K_2O or $K_2Cr_2O_4$.

$BaCO_3$ precipitates a mixture of the hydroxide and basic carbonate. Complete precipitation only after some hours.

K_2CO_3 and **Na_2CO_3** give a similar precipitate, the composition of which varies with the conditions of precipitation.

$(NH_4)_2S$ precipitates $Cr_2(HO)_6$. Precipitation complete. [Cr, like Al, is incapable of forming a sulphide in the wet way.]

Oxidation of Chromic Compounds.—By means of suitable oxidising agents, chromic compounds are readily converted into compounds of chromic acid, the mechanism of the change in all cases being the oxidation of the sesquioxide into the trioxide; thus—

$$Cr_2O_3 + 3O = 2CrO_3$$

One method, namely, by fusion with oxidising agents, has been explained under *Dry reactions*. The Cr_2O_3 in that instance is oxidised into the potassium salt of chromic acid. The oxidation may be accomplished in the wet way by the following reactions:—

(1) Boiling chromic hydroxide with potassium hydroxide and manganese dioxide—

$$Cr_2(HO)_6 + 4KHO + 6MnO_2 = 2K_2CrO_4 + 3Mn_2O_3 + 5H_2O$$

(2) By substituting lead peroxide for manganese dioxide—

$$Cr_2(HO)_6 + 4KHO + 3PbO_2 = 2K_2CrO_4 + 3PbO + 5H_2O$$

In this case secondary reactions take place, for PbO is soluble in KHO, and the solution so formed then reacts upon the K_2CrO_4, producing $PbCrO_4$, which also dissolves in KHO.

(3) By the action of hypochlorites (or hypobromites) in the presence of caustic alkalies, either employed as such, or formed in the solution by the use of chlorine or bromine in the presence of the caustic alkali—

$$Cr_2(HO)_6 + 4KHO + 3KClO = 3KCl + 2K_2CrO_4 + 5H_2O$$

(4) By the action of sodium peroxide. If a small quantity of Na_2O_2 be added to chromium hydroxide suspended in water, and the mixture gently warmed, the chromium compound is immediately converted into the yellow sodium chromate; thus—

$$Cr_2(HO)_6 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaHO + 2H_2O$$

β. **Chromic Acid and Chromates.**—The acid, H_2CrO_4, has never been isolated. The anhydride, CrO_3, is readily obtained by

They are known as *chromites*. Chrome iron ore is ferrous chromite, Cr_2O_3,FeO. Although analogous to the alumin*ates*, they must not be called chrom*ates*, as this name is reserved for the salts of chromic acid.

adding strong H_2SO_4 to a cold strong solution of potassium dichromate, when the oxide is deposited in the form of red silky needles. It forms two classes of salts, viz. the normal chromates, of which K_2CrO_4 is a type; and the dichromates,* of which $K_2Cr_2O_7$ is a familiar example. The chromates are mostly yellow or red in colour, and those which are soluble in water (see p. 40) impart a yellow or orange colour to the liquid. The most important of the insoluble chromates made use of in analysis, and which are all precipitated by the addition of potassium chromate to solutions of the metallic salts, are the following:—

Barium chromate, $BaCrO_4$ (see Ba reactions, p. 31).

Lead chromate, $PbCrO_4$ (see Pb reactions, p. 81).—$PbCrO_4$ melts without decomposition, and solidifies on cooling to a brown crystalline mass. At higher temperatures it gives off oxygen—

$$2PbCrO_4 = Cr_2O_3 + 2PbO + 3O$$

$PbCrO_4$ (known as *chrome yellow*), when digested with NaHO, or with K_2CrO_4, is converted into a red basic lead chromate (known as *chrome red*)—

$$2PbCrO_4 + 2NaHO = Na_2CrO_4 + H_2O + Pb_2CrO_5 \text{ (or } PbCrO_4,PbO)$$
$$2PbCrO_4 + K_2CrO_4 = PbCrO_4,PbO + K_2CrO_4,CrO_3$$

Silver chromate, Ag_2CrO_4.—A dark chocolate-red precipitate, soluble in ammonia and nitric acid.

Mercurous chromate (basic), Hg_2CrO_4,Hg_2O.—A brick-red precipitate, which, when dried, and heated in a tube, gives a mercury sublimate, evolves oxygen, and leaves a residue of Cr_2O_3.

Oxidation of Chromic Acid.—Although CrO_3 is such a highly oxygenated compound, it appears to be capable of still further oxidation by hydrogen peroxide, giving rise to a compound which is believed by some to be perchromic acid, $HCrO_4$, or $2CrO_3,H_2O_2$, and by others to be a compound of CrO_3 and H_2O_2 in undetermined proportions. The interest of the compound lies in the fact that it has an intense azure-blue colour, and its formation affords an extremely delicate test for either chromic acid or hydrogen peroxide. A few drops of H_2O_2 (or a few particles of

* The constitution of the dichromates (sometimes wrongly called *bi*chromates) may be expressed thus, K_2CrO_4,CrO_3. They are strictly analogous to the pyrosulphates, $K_2S_2O_7$, or K_2SO_4,SO_3, and on this account should consistently be named *pyrochromates*. By the action of strong acids, the normal potassium chromate is converted into the dichromate; thus, $2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2CrO_4,CrO_3$. And the dichromate is re-converted into the normal salt by the action of potash—

$$K_2CrO_4,CrO_3 + 2KHO = 2K_2CrO_4 + H_2O$$

Na_2O_2) are added to half a test-tube of water, and the mixture acidified with one or two drops of HCl. A single drop of potassium dichromate solution added to this produces an intense blue colour. [The compound is very unstable in aqueous solution, but less so in ether ; therefore, in testing for very minute quantities, ether should be added before the dichromate ; and on shaking the mixture, the ethereal layer which rises to the surface will be coloured blue.]

Reduction of Chromic Acid.—CrO_3 is a powerful oxidising agent, giving up oxygen to oxidisable substances, and being itself *reduced* to Cr_2O_3 ; that is, to the condition of a "chromic" compound. Thus, by sulphur dioxide it is reduced to chromium sulphate—

$$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3$$

The same action takes place in an acidified solution of potassium dichromate—

$$K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

Similarly, chromic acid and chromates are reduced by HCl, oxidising the hydrogen of the acid, and liberating chlorine, after the manner of peroxides ; thus—

$$CrO_3 + 6HCl = CrCl_3 + 3H_2O + 3Cl$$
$$K_2Cr_2O_7 + 14HCl = 2CrCl_3 + 2KCl + 7H_2O + 3Cl_2$$

On account of this reaction, a mixture of potassium dichromate and hydrochloric acid is capable of "oxidising" $FeCl_2$ into $FeCl_3$; $SnCl_2$ into $SnCl_4$; As_2O_3 into As_2O_5. In all cases of oxidation by chromic acid, the reduction of the chromic acid compound to the state of a "chromic" compound is evidenced by the change of colour from the yellow or orange of the former, to the green colour of the latter. This reduction and change of colour is at once seen by passing sulphuretted hydrogen through acidified potassium dichromate—

$$K_2Cr_2O_7 + 3H_2S + 8HCl = 2CrCl_3 + 2KCl + 7H_2O + 3S$$

Many organic substances also reduce chromic acid, such as oxalic acid, and alcohol. Thus, one molecule of oxalic acid, $C_2H_2O_4$, requires one atom of O to convert it into CO_2 and H_2O—

$$C_2H_2O_4 + O = 2CO_2 + H_2O$$

Potassium dichromate, in being reduced, has three available atoms of oxygen to give up; thus, $K_2Cr_2O_7 = Cr_2O_3,K_2O,3O$ (in the presence of dilute acids the Cr_2O_3 and K_2O form salts). Therefore

one molecule of $K_2Cr_2O_7$ can oxidise three molecules of oxalic acid, resulting in the evolution of six molecules of CO_2; thus—

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_2O_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6CO_2$$

If alcohol be added to a mixture of potassium dichromate and sulphuric acid, the alcohol (C_2H_6O) is oxidised first to aldehyde, C_2H_4O, and then to acetic acid ($C_2H_4O_2$), and the colour of the mixture changes from orange-red to green.

Iron, Fe.

Dry Reactions.—Iron compounds impart to a borax bead heated in the outer flame, a colour which appears chocolate when hot, and yellow when cold. After heating in the reducing flame, the colour changes to a bottle-green (the green colour of common bottle glass is caused by the presence of iron). When heated on charcoal with Na_2CO_3 in the inner blowpipe flame, iron compounds become reduced, and a dark grey magnetic mass is obtained. If this be washed with water in a small mortar, and the end of a magnet applied, it will be attracted after the manner of iron filings.

Wet Reactions.—The salts of iron are derived from the two oxides FeO and Fe_2O_3.* They are both basic oxides, and give rise to two classes of salts, namely, *ferrous* and *ferric* respectively. Ferrous salts readily take up oxygen, and become converted into ferric compounds; while the latter, under the influence of suitable reducing agents, easily pass back again to the ferrous condition.

(*a*) **Ferric Compounds.**—The common ferric salts that are soluble in water are the chloride, $FeCl_3$; nitrate, $Fe_2(NO_3)_6$, and sulphate, $Fe_2(SO_4)_3$. These all give yellowish-brown solutions.

NH_4HO, KHO, and NaHO throw down a brown voluminous precipitate of ferric hydroxide,† $Fe_2(HO)_6$, insoluble in excess, or in NH_4Cl.‡

K_2CO_3, Na_2CO_3, and $BaCO_3$ give the same precipitate, CO_2 being liberated—

$$2FeCl_3 + 3Na_2CO_3 + 3H_2O = Fe_2(HO)_6 + 6NaCl + 3CO_2$$

* The oxide known as *magnetic oxide of iron*, or ferroso-ferric oxide, Fe_3O_4 or Fe_2O_3,FeO, yields a mixture of ferric and ferrous salts.

† Several hydrated ferric oxides are known, *e.g.* $Fe_2O_3,3H_2O$; $Fe_2O_3,2H_2O$; Fe_2O_3,H_2O. Common rust of iron has the composition $2Fe_2O_3,3H_2O$. The composition of the precipitate produced by alkalies depends upon the conditions of precipitation.

‡ See footnote on p. 39, as to the influence of organic compounds.

The precipitate is soluble in a concentrated solution of K_2CO_3, giving a deep reddish solution of unknown composition. On the addition of water the hydroxide is reprecipitated. (With $BaCO_3$ basic carbonates are also precipitated.)

$(NH_4)_2S$ produces a black precipitate of *ferrous* sulphide. The action may be considered as taking place in two stages: (1) the reduction of the iron to the ferrous state, and (2) the formation of the ferrous sulphide; thus, using a dissected formula for ammonium sulphide—

$$(1)\quad \begin{matrix}\cdot\cdot & & \cdot\cdot\\ :NH_3 & NH_3: \\ \cdot\cdot & & \cdot\cdot\end{matrix} H_2S + 2FeCl_3 = 2FeCl_2 + 2HCl + S$$

$$(2)\quad (NH_4)_2S + FeCl_2 = FeS + 2NH_4Cl$$

In the first equation the hydrochloric acid formed unites with the ammonia, producing $2NH_4Cl$.

Sulphuretted hydrogen, H_2S, brings about the first stage in the above action, reducing the iron from the *ferric* to the *ferrous* state with precipitation of sulphur, but in the presence of the free acid which is developed by the action, ferrous sulphide cannot be formed. [*Ferric sulphide cannot be produced in the wet way.*]

Potassium ferrocyanide, $K_4Fe(CN)_6$, or K_4FeCy_6,* produces with ferric salts a dark blue precipitate (*Prussian blue*)—

$$3K_4(FeCy_6) + 4FeCl_3 = 12KCl + Fe_4(FeCy_6)_3$$

This test is extremely delicate, but where the amount of iron is very small, a blue or greenish coloration only is produced. "Prussian blue" is insoluble in hydrochloric acid, but readily dissolves in oxalic acid. It is decomposed by NaHO or KHO, with precipitation of ferric hydroxide—

$$Fe_4(FeCy_6)_3 + 12KHO = 2Fe_2(HO)_6 + 3K_4(FeCy_6)$$

Potassium ferricyanide, $K_3(FeCy_6)$, gives no precipitate with ferric salts.

Potassium thiocyanate, K(CN)S, produces with ferric salts a rich wine-red coloration, owing to the formation of ferric thiocyanate, $Fe(CNS)_3$, which is soluble in water. The colour of

* "Cy" is a recognised and convenient symbol for the radical (CN); cyanogen. The use of this reagent as a test for iron is unique, as being the only case in which the reagent is itself a compound containing the very metal it is employed to detect. The ferrocyanides and the ferricyanides, however, although compounds of iron, contain the metal in such a form of combination that it is not detected by the ordinary reagents. Before the iron in these compounds will give any of the ordinary reactions, its union with the cyanogen radical must be first destroyed (see Cyanides, p. 163).

this compound is very intense, hence the reaction may be employed to detect very small quantities of iron.*

Reduction of Ferric to Ferrous Compounds.—Ferr*ic* compounds are readily reduced to the ferr*ous* state; they are therefore oxidising agents of some importance. The action of $(NH_4)_2S$ and of H_2S has been already mentioned. Nascent hydrogen reduces them in the same way; therefore, when metallic iron is dissolved in HCl or H_2SO_4, the salts produced are ferrous chloride and sulphate respectively. Nitric acid, on the other hand, converts the iron into the "ferric" state.

A ferric salt already in solution is reduced by nascent hydrogen, generated by introducing zinc into the acidified liquid.

In passing from $FeCl_3$ to $FeCl_2$, one atom of chlorine is available for oxidising purposes, and is capable of bringing about such actions as the following—

The "oxidation" of stannous chloride, $SnCl_2$, to stannic chloride, $SnCl_4$.

The oxidation of sulphurous acid or thiosulphuric acid into sulphuric acid; thus—

$$2FeCl_3 + H_2SO_3 + H_2O = H_2SO_4 + 2HCl + 2FeCl_2$$
$$2FeCl_3 + Na_2SSO_3 + H_2O = Na_2SO_4 + 2HCl + 2FeCl_2 + S$$

(*b*) **Ferrous Compounds.**—Ferrous salts are usually pale green when crystallised, and white when anhydrous. Of the common salts the chloride and sulphate are soluble. The latter readily forms double salts with the sulphates of the alkalies (such as ferrous ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$), which are also soluble in water, and are less readily oxidised on exposure to the air than ferrous sulphate, which they otherwise closely resemble in appearance.

NH_4HO, KHO, and NaHO produce a precipitate of ferrous hydroxide, $Fe(HO)_2$, which is at first a dirty white colour, but which rapidly turns first pale greenish-grey, then a dirty grey, and finally brown, owing to its oxidation by atmospheric oxygen. The presence of ammonium salts renders the precipitation incomplete. The

* This is a "reversible" reaction, and therefore, when equilibrium is established, there will be present in the liquid both ferric chloride and potassium thiocyanate, thus, $3KCNS + FeCl_3 \rightleftarrows 3KCl + Fe(CNS)_3$. That this is so may be proved by the following experiment: Add to a little moderately dilute ferric chloride a small quantity of potassium thiocyanate; then dilute the liquid with water so that the intensity of the red colour is greatly reduced, and divide it into two portions. To one add more ferric chloride, and to the other add more potassium thiocyanate. In each case the liquid becomes a deeper red colour.

precipitate is not soluble in excess of the reagents; boiling with KHO turns it black, converting it into Fe_3O_4.

K_2CO_3 and Na_2CO_3 give a white precipitate of ferrous carbonate, $FeCO_3$, which on exposure to the air quickly absorbs oxygen.

$(NH_4)_2S$ precipitates black ferrous sulphide, FeS. Readily soluble in acids, with evolution of sulphuretted hydrogen; insoluble in alkalies. The precipitate in the moist state is oxidised on exposure to the air into ferrous and basic ferric sulphate.

$K_4(FeCy_6)$ precipitates potassium ferrous ferrocyanide, $FeK_2(FeCy_6)$, thus—

$$K_4(FeCy_6) + FeCl_2 = 2KCl + FeK_2(FeCy_6)$$

When the solutions are mixed in test-tubes in the ordinary way, the precipitate has a greenish-blue colour; but when the reaction is made in an atmosphere free from oxygen, and the solutions are previously boiled so as to entirely expel all dissolved oxygen, the precipitate is perfectly white. It rapidly absorbs oxygen and becomes blue, and is also easily oxidised to "Prussian" blue by nitric acid or chlorine; thus—

$$4FeK_2(FeCy_6) + 2Cl_2 = Fe_4(FeCy_6)_3 + K_4FeCy_6 + 4KCl$$

Potassium ferricyanide, $K_3(FeCy_6)$, gives, with ferrous salts, a precipitate of ferrous ferricyanide, $Fe_3(FeCy_6)_2$ (known as *Turnbull's blue*), which is indistinguishable by its appearance from *Prussian* blue—

$$2K_3(FeCy_6) + 3FeCl_2 = Fe_3(FeCy_6)_2 + 6KCl$$

The precipitate is insoluble in hydrochloric acid, but is decomposed by caustic alkalies, with the precipitation of ferrous hydroxide; thus—

$$Fe_3(FeCy_6)_2 + 6KHO = 2K_3(FeCy_6) + 3Fe(HO)_2$$

Oxidation of Ferrous to Ferric Compounds.—The ferric salts being the more stable, the ferrous compounds undergo oxidation even more readily than the ferric salts become reduced. Mere exposure to the air in many cases causes the change. In analysis the oxidation is usually accomplished either by chlorine (or bromine) or by nitric acid.

The chlorine may be employed in the form of its aqueous solution (*chlorine water*), or more conveniently by generating the gas in contact with the ferrous compound by means of hydrochloric acid and potassium chlorate. The solution of the ferrous salt is acidified with concentrated HCl, and heated. A few particles of

potassium chlorate are then dropped into the mixture, and the heating continued for a short time.

A mixture of HCl and $KClO_3$ evolves both chlorine and chlorine peroxide ; thus—

$$4KClO_3 + 12HCl = 6H_2O + 4KCl + 3ClO_2 + 9Cl$$

Both the free chlorine and the chlorine of the chlorine peroxide are available for oxidising the ferrous compound ; hence the equation may be simplified as follows :—

$$KClO_3 + 6HCl + 6FeCl_2 = 6FeCl_3 + KCl + 3H_2O$$

When the oxidation is accomplished with nitric acid, the strong acid is added, a few drops at a time, to the hot acidulated solution of the ferrous salt. The solution becomes dark in colour, and nitric oxide is disengaged ; thus—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$
$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + 2H_2O + NO$$

Unless the solution of the ferrous salt is acidified, a portion of the iron is converted into Fe_2O_3, which is taken up, in the case of the sulphate, by the ferric sulphate, forming insoluble basic ferric sulphates, $Fe_2(SO_4)_3$, xFe_2O_3.

Separation of the Metals of Group IIIA.

The separation of the metals of this subdivision from the other metals of Group III., and also from those of Groups IV. and V., is based upon the fact that their hydrated sesquioxides are precipitated by ammonia in the presence of ammonium chloride.*

The separation of the three metals of this group from each other is based upon—

1. The oxidation of chromic oxide to chromic acid ; and
2. The solubility of aluminium hydroxide in caustic alkalies.

To the solution add NH_4Cl in considerable quantity ; heat the mixture to boiling, and add NH_4HO carefully until precipitation is complete. Bring the liquid once more "to the boil," when, if sufficient ammonia has been added, the steam will smell of it. Filter the mixture while hot.†

* The separation of Group IIIA. from Group IIIB. by means of NH_4HO is not sharp and complete in all cases (see Manganese reactions).

† In the regular course of a complete analysis, the filtrate obtained here will contain the metals of Group IIIB., IV., and V.

The **precipitate** consists of $Al_2(HO)_6$, $Cr_2(HO)_6$, and $Fe_2(HO)_6$. Wash the precipitate, and transfer it (or a portion of it) to a test-tube with a small quantity of water. Add to the mixture a little sodium peroxide, and boil for a moment, until the temporary effervescence ceases. The chromium is oxidised to chromate, and the $Al_2(HO)_6$ dissolves in the NaHO, which is formed by the action of the sodium peroxide upon the water. Filter.

The **filtrate** contains sodium chromate, Na_2CrO_4, and sodium aluminate, $Al_2O_3,3Na_2O$. The former shows itself by the yellow colour. Divide into two portions—

(1) Acidify with acetic acid, and confirm **chromium** by special reactions, *e.g.* lead acetate.

(2) Acidify with dilute nitric acid, and add NH_4HO. A white precipitate of $Al_2(HO)_6$ confirms **aluminium**.

The **residue** consists of $Fe_2(HO)_6$. Dissolve in a little hot dilute HCl, and confirm **iron** by special reactions, *e.g.* K_4FeCy_6 or KCNS.*

The following alternative methods of separation may also be used.

(*a*) The precipitated hydroxides are washed and dried. The residue is then mixed with at least six times its weight of *fusion mixture*,† and fused in a platinum capsule. In this way the chromium is converted into alkaline chromate ; a variable proportion of the aluminium into aluminates.

The fused mass is then dissolved in water, and filtered. The filtrate is tested for aluminium and chromium, while the residue is dissolved and tested for iron, as in the foregoing scheme.

(*b*) The precipitated hydroxides are dissolved in a little warm dilute HCl, and pure NaHO‡ added in quantity considerably more than sufficient to produce precipitation. The mixture is then boiled for a few minutes, and filtered.

* At this stage in the process, the iron will be in the "ferric" condition. To ascertain whether it was originally present as a "ferrous" or "ferric" compound, separate tests must be made in the solution *before* it has been subjected to the action of either reducing or oxidising agents.

† *Fusion mixture* is a mixture of Na_2CO_3 and K_2CO_3 in equivalent proportions (or about 10 parts Na_2CO_3 to 13 of K_2CO_3). It is used in preference to Na_2CO_3 alone, because it has the property of melting more easily than either carbonate separately.

‡ The commercial caustic soda usually employed in the laboratory always contains more or less sodium aluminate. The student should test a sample of the reagent by neutralising it with HCl, and then adding NH_4HO. In the method of separation given above, this difficulty is avoided, as the sodium peroxide of commerce is usually free from this impurity.

The filtrate contains sodium aluminate, $Al_2O_3,3Na_2O$. Add dilute HCl until just acid, and reprecipitate $Al_2(HO)_6$ with ammonia.

The precipitate contains $Cr_2(HO)_6$ and $Fe_2(HO)_6$. This is dried, and fused with fusion mixture. The fused mass is dissolved in water and filtered. The solution contains sodium chromate, while the Fe_2O_3 remains on the filter. These are confirmed as in the above methods.

CHAPTER VI.

Reactions of the Metals of Group III.—Division B.

Manganese, Mn.

Dry Reactions.—Manganese compounds, when heated in a borax bead in the oxidising flame, impart to the bead a violet or lilac colour. When heated in the reducing flame, the bead again becomes colourless.

A more characteristic reaction is based upon the oxidation of manganese to manganic acid. When a manganese compound is fused with KHO, or with Na_2CO_3 and a little KNO_3 or $KClO_3$ upon a platinum capsule, the manganese undergoes oxidation, and a deep green-coloured mass is obtained, consisting of manganates of the alkali metals—

$$MnO_2 + Na_2CO_3 + O \text{ (from } KClO_3 \text{ or } KNO_3) = Na_2MnO_4 + CO_2$$
$$MnO_2 + 2KHO + O = K_2MnO_4 + H_2O$$

The green mass (especially when obtained by fusion with KHO) dissolves in a small quantity of cold water to a deep green solution. When this is either acidified, or warmed, or even largely diluted with water, its colour changes from green to pink, owing to the conversion of the manganate into permanganate; thus—

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KHO + MnO_2$$

Wet Reactions.—Of the oxides of manganese two are basic: the monoxide, MnO, giving rise to the mangan*ous* salts; and the sesquioxide, Mn_2O_3, to the mangan*ic* salts.

[The oxide, Mn_3O_4, yields both manganous and manganic salts; while MnO_2 gives manganous salts with the elimination of available oxygen.]

The manganic salts are extremely unstable in solution, and are incapable of existing as such under the ordinary conditions of analysis. Thus the chloride, believed to have the composition Mn_2Cl_6, passes at ordinary temperatures into $MnCl_2$ and chlorine.

Of the common manganous salts, the chloride, $MnCl_2$, $4H_2O$, and the sulphate, $MnSO4,5H_2O$, are soluble in water. In the crystallised state they have all a pink colour. Manganous salts which are soluble in water do not undergo atmospheric oxidation.

NH_4HO, KHO, and NaHO produce a white precipitate of manganous hydroxide, $Mn(HO)_2$. Insoluble in excess of the reagent, the precipitate quickly absorbs oxygen, and is converted into hydrated manganic oxide, Mn_2O_3,H_2O, having a brown colour.

Freshly precipitated $Mn(HO)_2$, while still white, is soluble in NH_4Cl, forming the soluble double salt $MnCl_2,2NH_4Cl,H_2O$; therefore in the presence of NH_4Cl, manganous hydroxide is not precipitated by NH_4HO, and only incompletely by KHO or NaHO.

The ammoniacal solution of the double chloride, however, is capable of absorbing oxygen just as the precipitated $Mn(HO_2)$ does, and the liquid quickly becomes muddy, owing to the precipitation from it of the brown hydrated manganic oxide.*

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ give a white precipitate of manganous carbonate, $MnCO_3$; insoluble in excess. The precipitation is not complete in the presence of NH_4Cl. Manganous carbonate absorbs atmospheric oxygen, and is slowly changed into the brown hydrated oxide.

$(NH_4)_2S$ precipitates manganous sulphide, MnS, as a pale pinkish-white compound, easily soluble in dilute acids (*distinction from* Ni *and* Co), soluble also in acetic acid (*distinction from* Zn). Precipitation with $(NH_4)_2S$ is only complete in the presence of NH_4Cl. Owing to the ready solubility of MnS in acids, H_2S is incapable of precipitating manganous sulphide from neutral solutions ; for, by double decomposition, the acid of the manganous salt would be set free, and would immediately redissolve the sulphide.

Manganese Compounds as Oxidising Agents.—When manganese dioxide is acted upon by acids, a manganous salt is

* It is this characteristic property of the double manganous ammonium chloride that renders the complete separation of this metal from those of Group IIIA. extremely difficult to accomplish. The hydrated oxides of Al, Cr, and Fe are sure to carry down more or less of the manganese along with them, and a *small* quantity of manganese, in the presence of a large proportion of iron, might in this way be altogether overlooked. If the precipitation with NH_4HO of Group IIIA., be made as quickly as possible in a hot solution, and the excess of ammonia at once boiled off, and the liquid filtered immediately, the risk of precipitating the manganese may be reduced to a minimum. The student will do well to practise the separation of manganese from the metals of Group IIIA. by using solutions containing known small proportions of a manganous salt, mixed with large quantities of iron or chromium or aluminium.

formed, and available oxygen is eliminated, which either appears as free oxygen gas, or as the product of the oxidation of the acid ; thus—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

The other oxides of manganese, higher than the monoxide, may be regarded as compounds of MnO_2 with MnO in different proportions, and when acted upon by hydrochloric acid they also yield manganous chloride and chlorine, the amount of chlorine being the measure of the amount of MnO_2 in the compound—

$$Mn_3O_4 \text{ or } 2MnO,MnO_2 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2$$
$$Mn_2O_3 \text{ or } MnO,MnO_2 + 6HCl = 2MnCl_2 + 3H_2O + Cl_2$$

Nitric acid (free from *nitrous acid*) has no action upon manganese dioxide ; when, therefore, one of these other oxides is acted upon by nitric acid, the monoxide is converted into the nitrate, and the dioxide is left ; thus—

$$Mn_2O_3 \text{ or } MnO,MnO_2 + 2HNO_3 = Mn(NO_3)_2 + H_2O + MnO_3$$

The manganates and permanganates are still more powerful oxidising agents. When these are acted upon by sulphuric acid, we may suppose that the hypothetical manganic and permanganic acids are first liberated, which, being incapable of existence, break up into the unstable oxides MnO_3 and Mn_2O_7 ; and that these in contact with sulphuric acid form manganous sulphate, with the evolution of oxygen ; thus—

$$\begin{cases} K_2MnO_4 + H_2SO_4 = K_2SO_4 + H_2MnO_4 (= H_2O + MnO_3) \\ MnO_3 + H_2SO_4 = MnSO_4 + H_2O + O_2 \end{cases}$$
$$\begin{cases} 2KMnO_4{}^* + H_2SO_4 = K_2SO_4 + 2HMnO_4 (= H_2O + Mn_2O_7) \\ Mn_2O_7 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + 5O \end{cases}$$

From these equations, it will be seen that from one molecule of the manganate two atoms of oxygen are given off, while two molecules of the permanganate evolve five atoms of oxygen. When acted upon by hydrochloric acid, the equivalent quantity of chlorine is evolved—

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl$$

Potassium permanganate is therefore a most important oxidising material. In the presence of hydrochloric or sulphuric acid, it is

* Some chemists prefer to use the double formula, $K_2Mn_2O_8$, for potassium permanganate.

capable of oxidising almost every oxidisable compound. The following may be taken as typical examples :—

(1) Sulphurous acid to sulphuric acid—

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 3H_2O + 2H_2SO_4$$

(2) Oxalic acid to carbon dioxide and water—

$$H_2C_2O_4 + O = H_2O + 2CO_2$$

One atom of oxygen is required for the oxidation of one molecule of oxalic acid ; therefore the five atoms of oxygen derivable from two molecules of permanganate will oxidise five molecules of oxalic acid.

(3) Ferrous sulphate to ferric sulphate, in the presence of free sulphuric acid—

$$2\ FeSO_4 + H_2SO_4 + O = H_2O + Fe_2(SO_4)_3$$

One molecule of $KMnO_4$ is therefore capable of oxidising five molecules of $FeSO_4$; or, in the presence of HCl, of oxidising five molecules of $FeCl_2$ into $FeCl_3$.*

In all these cases of oxidation the change is accompanied by the destruction of the violet colour of the permanganate ; hence it is perfectly easy to watch the progress of the action, and to ascertain the exact moment when the process is complete.

Zinc, Zn.

DRY REACTIONS.—Zinc compounds give no characteristic borax bead.

When heated on charcoal with sodium carbonate in the reducing

* Two powerful oxidising substances are often able to oxidise each other in such a way that at first sight it would seem that they were playing the part of reducing agents. Thus, when potassium permanganate and hydrogen peroxide are brought together, both compounds are *reduced.* The available oxygen from the permanganate *oxidises the available oxygen* of the hydrogen peroxide, with the result that a number of *oxidised atoms of oxygen* (*i.e.* complete molecules) are set free. In the presence of H_2SO_4, the five oxygen atoms available in two molecules of permanganate oxidise five available atoms of oxygen contained in as many molecules of hydrogen peroxide ; thus—

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 5H_2O + 3H_2O + K_2SO_4 + 2MnSO_4 + 5O_2$$

In the absence of the free acid, hydrated sesquioxide of manganese is precipitated, which then becomes a catalytic agent, being alternately oxidised and reduced again—

$$2KMnO_4 + 4H_2O_2 = 2KHO + Mn_2O_3,H_2O + 2H_2O + 4O_2$$

$$\begin{cases} Mn_2O_3 + H_2O_2 = H_2O + 2MnO_2 \\ 2MnO_2 + H_2O_2 = H_2O + O_2 + Mn_2O_3 \end{cases}$$

flame, zinc compounds are reduced, but the metal is too volatile to appear in the form of globules. As it is reduced, it volatilises ; and the vapour burns as it passes through the outer flame, which thereby becomes tinged a bluish-white colour. The zinc oxide which is thus produced, deposits as an incrustation upon the charcoal, which is canary-yellow while hot, becoming white on cooling. Zinc oxide is not volatile, and therefore the incrustation does not disappear when the oxidising flame is made to play upon it. If the zinc oxide be moistened with a drop of cobalt nitrate, and again heated in the oxidising flame, it assumes a green colour.

WET REACTIONS.—Zinc forms only one series of salts, derived from the only oxide, ZnO.

Of the common salts the chloride, sulphate, and nitrate are soluble in water.

NH_4HO, KHO, or NaHO throws down a white precipitate of $Zn(HO)_2$, readily soluble in excess of the reagent, forming double salts (sometimes called *zincates*), such as $ZnNa_2O_2$.* Moderately strong solutions of these zincates may be boiled without undergoing any change, but from dilute solutions $Zn(HO)_2$ is reprecipitated. $Zn(HO)_2$ is soluble in NH_4Cl, owing to its readiness to form soluble double salts with the alkaline chlorides, having the general formula $ZnCl_2,2RCl$—

$$Zn(HO)_2 + 4NH_4Cl = ZnCl_2,2NH_4Cl + 2NH_4HO$$

Hence in the presence of much ammonium chloride, NH_4HO gives no precipitate, and the precipitation with KHO or NaHO is incomplete.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ produces a white precipitate of basic carbonate, the composition of which varies with conditions of precipitation, $x ZnCO_3$, $y Zn(HO)_2$, $n H_2O$.† The precipitate is soluble in excess of $(NH_4)_2CO_3$. The presence of much NH_4Cl partially or entirely prevents the precipitation.

* Upon this property is based the separation of zinc from Mn, Ni, and Co, but the solubility of $Zn(HO)_2$ in caustic alkalies is rendered less easy by the presence of the hydroxides of Mn, Ni and Co, owing to the tendency of these to unite with the zinc oxide to form compounds which are difficultly decomposed by the alkali.

† $3ZnCl_2 + 3Na_2CO_3 + 5H_2O = ZnCO_3,2Zn(HO)_2,H_2O \quad 6NaCl + 2CO_2$,
$5ZnCl_2 + 5Na_2CO_3 + 8H_2O = 2ZnCO_3,3Zn(HO)_2,5H_2O + 10NaCl + 3CO_2$

The former of these basic carbonates is known in pharmacy as *zinci carbonas*.

The normal zinc carbonate is precipitated by hydrogen sodium carbonate. We may suppose that the acid which is in this case liberated, prevents the formation of the hydroxide—

$$ZnCl_2 + HNaCO_3 = ZnCO_3 + HCl + NaCl$$

The precipitate is soluble also in a concentrated solution of K_2CO_3, but is reprecipitated on dilution with water (compare Fe, Ni, Co).

$(NH_4)_2S$ throws down a white precipitate of zinc sulphide, ZnS. In the presence of NH_4Cl the precipitation is complete even from dilute solutions. ZnS is soluble in dilute mineral acids, hence H_2S is incapable of completely precipitating this sulphide from neutral solutions of the zinc salts of such acids—

$$ZnCl_2 + H_2S \rightleftarrows ZnS + 2HCl$$

ZnS is insoluble in acetic acid (contrast MnS), therefore from the acetate, *or other zinc salts in presence of an alkaline acetate*, ZnS is completely precipitated by H_2S; thus—

$$Zn(C_2H_3O_2)_2 + H_2S = ZnS + 2H(C_2H_3O_2)$$
$$ZnCl_2 + 2Na(C_2H_3O_2) + H_2S = ZnS + 2NaCl + 2H(C_2H_3O_2)$$

Nickel, Ni.

Dry Reactions.—Nickel compounds impart a dark red-brown colour to the borax bead when heated in the oxidising flame, the colour becoming brownish-yellow on cooling. In the reducing flame the borax bead becomes opaque and grey. In a bead of microcosmic salt, the red-brown colour persists in both flames.

The presence of other colour-producing oxides renders this test uncertain, while even traces of cobalt entirely mask it. Heated on charcoal with Na_2CO_3, metallic nickel is obtained as a grey feebly magnetic mass.

Wet Reactions.—Only one of the oxides of nickel is basic, namely NiO, hence only one series of salts exists. The sesquioxide, Ni_2O_3, behaves like a peroxide; thus—

$$Ni_2O_3 + 2H_2SO_4 = 2NiSO_4 + 2H_2O + O$$

In the crystalline or hydrated condition the nickel salts have a green colour, and dissolve to green solutions. The anhydrous salts are pale yellow. Of the common salts, the chloride, nitrate, and sulphate are soluble in water. Nickel salts form a number of soluble double salts; those with ammonium salts being important.

KHO or NaHO gives a pale bluish-green precipitate of nickelous hydroxide, $Ni(HO)_2$,* insoluble in excess of either reagent; soluble

* The composition of the precipitate is more exactly expressed by the formula $4Ni(HO)_2, H_2O$. When dried and strongly heated, it is converted into NiO.

in ammonium salts. $Ni(HO)_2$ is not oxidised on exposure to air, but it is converted into black hydrated sesquioxide, $Ni_2O_3,3H_2O$, by hypochlorites, or by the action of chlorine in the presence of caustic alkalies; thus—

$$2Ni(HO)_2 + NaClO + H_2O = NaCl + Ni_2O_3,3H_2O$$
$$2Ni(HO)_2 + 2NaHO + Cl_2 = 2NaCl + Ni_2O_3,3H_2O^*$$

NH_4HO forms a number of readily soluble double compounds with nickel salts. When added to an acid solution of a nickel salt, *e.g.* $NiSO_4$, no precipitate is produced, owing to the ready solubility of $Ni(HO)_2$ in ammonium salts. With *neutral* solutions partial precipitation takes place, the precipitate quickly dissolving in excess of ammonia to a greenish-blue solution. This blue liquid contains in solution the salt $NiSO_4,4NH_3$. The nickel in this solution is not oxidised by hypochlorites, but it is completely precipitated as $Ni(HO)_2$ by KHO.

K_2CO_3 or Na_2CO_3 produces a pale-green precipitate of basic carbonate, $xNiCO_3,yNi(HO)_2$.

The precipitate is soluble to a pale-green solution in a concentrated solution of K_2CO_3, but is reprecipitated on dilution with water.

$(NH_4)_2CO_3$ gives no precipitate in acid solutions, but from neutral solutions a similar compound is produced, which dissolves in excess of the reagent to a bluish solution.

$(NH_4)_2S$, or H_2S in presence of ammonia, produces a black precipitate of NiS, soluble to a slight extent in excess; more readily soluble if ammonia or polysulphides of ammonia are present, yielding a brown solution. From this solution the dissolved NiS is reprecipitated slowly on boiling, more quickly after acidifying with acetic acid, or the addition of ammonium acetate.

NiS is only difficultly soluble in strong HCl, and almost insoluble in the dilute acid; also in acetic acid. Readily soluble in *aqua*

* This higher oxide undergoes rapid alternate reduction and oxidation in the presence of the hypochlorite. As soon as it is formed it is acted upon by the hypochlorite, with evolution of oxygen; thus, formulating the oxides for simplicity—

$$Ni_2O_3 + NaClO = NaCl + 2NiO + O_2$$

The compound therefore becomes a *catalytic agent*, causing the evolution of oxygen from a relatively infinite quantity of a hypochlorite. Cobalt oxide behaves in the same way (see Methods of obtaining oxygen, Newth's "Inorganic Chemistry"). The hydrated sesquioxide behaves with acids in the same way as the anhydrous oxide; thus with HCl it yields chlorine—

$$Ni_2O_3,3H_2O + 6HCl = 2NiCl_2 + 6H_2O + Cl_2$$

regia, or in HCl and a crystal of $KClO_3$, yielding $NiCl_2$; soluble also in HNO_3.

H_2S only produces *complete* precipitation of NiS from a warm solution of the acetate, or from other nickel salts in the presence of an alkaline acetate. In the case of neutral solutions of nickel salts with mineral acids, the precipitation is only partial, while in acid solutions it does not take place at all.

Cobalt, Co.

Dry Reactions.—Cobalt compounds impart to a borax bead a rich blue colour, when heated either in the oxidising or reducing flame. The test is characteristic and delicate. Many metallic oxides which give coloured borax beads become either colourless or lighter in colour when heated in the reducing flame, hence when mixed with these, the blue colour of the cobalt becomes more visible after heating the bead in the inner flame.

Wet Reactions.—Cobalt forms a number of oxides, two only of which are basic. The *cobaltous salts* are derived from CoO, while the feebly basic sesquioxide Co_2O_3 forms the very unstable cobaltic salts.

Of the common cobaltous salts, the sulphate, nitrate, and haloid salts are soluble in water. In the hydrated condition they have a pink colour, dissolving to pink solutions. In the anhydrous state they are blue. A strong aqueous solution (pink) will, however, turn blue when boiled, and return to its original pink colour when again cooled. In alcohol, cobalt chloride dissolves to a deep blue solution, which turns pink on the addition of water.

KHO or NaHO gives a greenish-blue precipitate of a basic salt. On boiling with excess of the alkali, the precipitate is converted into the pink hydroxide, $Co(HO)_2$, which, however, is coloured more or less brown by the oxidation of a portion of it (by atmospheric oxygen) into the hydrated cobaltic oxide, $Co_2O_3{,}3H_2O$, or $Co_2(HO)_6$.

$Co(HO)_2$ is oxidised by hypochlorites, in the same manner as the corresponding nickel compound.

NH_4HO produces no precipitate in acid solutions. In neutral solutions it causes partial precipitation of a basic salt, which dissolves easily in excess. The solution, which has a brownish colour, absorbs oxygen, and becomes darker in colour.*

* Cobalt (in common with platinum and a few other metals) possesses the property of forming a large number of compounds with ammonia. These salts, which are many of them extremely complex in their constitution, and

K_2CO_3 or Na_2CO_3 precipitates a lilac-coloured basic carbonate, $xCoCO_3$, $yCo(HO)_2$.

The precipitate is soluble to a violet solution in a concentrated solution of K_2CO_3, but is reprecipitated on dilution with water (compare Co, Zn, Cu). In all these cases the solution is believed to contain a double carbonate, which is unable to exist in the presence of much water.

$HKCO_3$ gives a pinkish precipitate of normal cobalt carbonate, $CoCO_3$. The precipitate so obtained is soluble in hydrogen peroxide, yielding a deep *green* solution.* The production of this green solution constitutes a very delicate test for cobalt. It may be carried out in the following way ; to a strong solution of potassium (or sodium) bicarbonate, about an equal bulk of hydrogen peroxide is added. On the addition of a single drop of cobalt chloride, the green colour will appear.†

$(NH_4)_2CO_3$ gives no precipitate in acid solutions. In neutral solutions partial precipitation of basic carbonate takes place ; the precipitate readily dissolves in excess to a reddish solution.

$(NH_4)_2S$ gives a black precipitate of cobaltous sulphide, CoS. The precipitation is complete in the presence of NH_4Cl (contrast NiS). CoS is soluble in HNO_3, in "aqua regia," and in HCl with the addition of a crystal of $KClO_3$; difficultly soluble in strong HCl ; practically insoluble in dilute HCl.

H_2S precipitates CoS under the same conditions as apply in the case of NiS.

difficult to classify, are known as *cobaltamines*. The *ammonio-cobaltous* compounds easily absorb oxygen, and pass into the more complex and more numerous *ammonio-cobaltic* salts. Nickel does not form compounds corresponding to the *ammonio-cobaltic* salts.

* Durrant.

† The exact nature of this curious reaction has not yet been established. There is little doubt but that the cobalt is present in a higher state of oxidation than in Co_2O_3 ; probably the compound is a cobaltate corresponding to the ferrates and manganates. Carbon dioxide is evolved when it is produced, which may be explained by the equation—

$$CoCO_3 + 2H_2O_2 = H_2CoO_4 + CO_2 + H_2O$$

At the same time, the compound is able to act as a catalytic agent towards hydrogen peroxide, causing the evolution of oxygen to take place, the compound undergoing rapid alternate reduction and oxidation, in the same way as silver oxide behaves with hydrogen peroxide. The green colour of the solution, curiously enough, is indistinguishable by the eye from the green of nickel salts. Nickel is incapable of giving this reaction, hence it constitutes a ready means of detecting even traces of cobalt in the presence of nickel.

The Cyanides.

The metals of Group IIIB. all form compounds with cyanogen, some of which are of importance in analysis. The addition of potassium cyanide to solutions of either a manganous, zinc, nickel, or cobaltous salt results in the precipitation of the cyanide, of the general formula $R\overline{C}y_2$. In each case, also, the precipitated cyanide *readily dissolves* in excess of the KCy, producing double cyanides. In the case of Mn, Zn, and Ni, these have the general formula $2KCy,RCy_2$, or K_2RCy_4, while the cobalt double cyanide has the formula $4KCy,CoCy_2$ (or K_4CoCy_6, corresponding to potassium ferrocyanide, K_4FeCy_6).

From the solutions of these double cyanides, $(NH_4)_2S$ is incapable of precipitating the metals as sulphides. The addition of dilute HCl or H_2SO_4 to these solutions causes the reprecipitation of the cyanide—

$$2KCy,NiCy_2 + 2HCl = 2KCl + 2HCy + NiCy_2$$

In the case of the Mn, Zn, and Ni compounds, boiling with dilute acid completely decomposes the metallic cyanide ; thus—

$$2KCy,NiCy_2 + 4HCl = 2KCl + 4HCy + NiCl_2.$$

The chief interest attaching to these compounds in this connection, is due to the difference between the behaviour of cobalt and of nickel towards cyanogen. The double cyanide of potassium and cobalt, $4KCy,CoCy_2$ or K_4CoCy_6 (like the corresponding iron compound) exhibits a great readiness to undergo oxidation, and to pass from the condition of *cobaltocyanide* to *cobalticyanide ;* thus—

$$2K_4CoCy_6 + O + H_2O = 2KHO + 2K_3CoCy_6$$

Nickel forms no compounds corresponding to the cobalticyanides. When the nickel double cyanide is oxidised (*e.g.* by chlorine, bromine, or hypochlorites), the nickel is converted into the black hydrated sesquioxide and precipitated ; thus—

$$2K_2NiCy_4 + NaClO + 5H_2O = Ni_2O_3,3H_2O + NaCl + 4KCy + 4HCy$$

While under the same oxidising treatment, the cobalt double cyanide is converted into potassium cobalticyanide, which remains in solution, and can therefore be separated by filtration ; thus—

$$2K_4CoCy_6 + NaClO + H_2O = NaCl + 2KHO + 2K_3CoCy_6$$

The cobaltocyanides are so readily oxidised, that by merely boiling the aqueous solution the change is effected; thus—

$$K_4CoCy_6 + H_2O = KHO + K_3CoCy_6 + H$$

Owing to this reaction, the double cobalt cyanide does not behave, when boiled with dilute acid, in the same manner as the nickel double cyanide (see above). We may suppose that the cobalt cyanide first formed, in the presence of free HCy (liberated partly from the double cyanide and partly from the excess of KCy present) and water, is converted into cobalticyanic acid in the following manner :—

$$(1)\ 4KCy,CoCy_2 + 4HCl = 4KCl + 4HCy + CoCy_2$$
$$(2)\ CoCy_2 + 4HCy + H_2O = H_3CoCy_6 + H$$

It follows from this that the addition of dilute HCl to a solution of a cobalticyanide does not result in the precipitation of a cyanide, but only in the liberation of cobalticyanic acid.

The metal cobalt in cobalticyanides, like iron in ferricyanides, is not precipitated by the ordinary reagents for these metals.

Separation of the Metals of Group IIIB.

The separation of the four metals of this group is based upon—

1. The solubility of $Zn(HO)_2$ in caustic alkalies.
2. The solubility of MnS in acetic acid.
3. The different behaviour of the double cyanides of Ni and Co, when subjected to oxidising agents.

In the course of a systematic analysis, the metals of Group IIIB. are looked for in the solution after Group IIIA. has been separated by means of NH_4HO in the presence of NH_4Cl. H_2S is passed through this ammoniacal solution, whereby the sulphides of Mn, Zn, Ni, and Co are precipitated. The mixture is gently warmed and filtered.*

* Even when the exercise is confined only to Group IIIB., the student is advised to go through the step of precipitating the group as sulphides in the ammoniacal solution prepared as described on p. 48.

The **precipitate,** consisting of MnS, ZnS, NiS, and CoS, is dissolved in hot dilute HCl, with the aid of a few particles of $KClO_3$.* The solution is boiled until it no longer smells of chlorine, and NaHO added in excess. It is again boiled (to ensure the solution of all the $Zn(HO)_2$), and filtered after cooling (hot NaHO will attack the filter-paper).

The **solution** contains sodium zincate, $ZnNa_2O_2$.

Pass H_2S through the liquid (or add H_2S water), when a white precipitate of ZnS is produced.

The **precipitate,** consisting of $Mn(HO)_2$, $Ni(HO)_2$, and $Co(HO)_2$, is washed to remove the soluble zinc salt still adhering to it, and then dissolved in the smallest quantity of warm HCl. The solution is *nearly* neutralised with NH_4HO, a considerable quantity of ammonium acetate added, and H_2S passed through the mixture until precipitation is complete.

The **solution** contains manganous acetate, $Mn(C_2H_3O_2)_2$.

Precipitate $MnCO_3$ by adding Na_2CO_3. Filter; wash thoroughly; dissolve in HCl, and confirm Mn by precipitation of the pinkish MnS, with $(NH_4)_2S$ after NH_4Cl and NH_4HO.

The formation of the green manganate may also be used as a confirmatory test.

The **precipitate** (NiS and CoS). Test a small portion with a borax bead. Blue colour indicates cobalt. Dissolve the precipitate in the least quantity of *aqua regia;* boil off the excess of acid, and nearly neutralise with Na_2CO_3 (avoid dilution). Add KCy (freshly made solution) until the precipitated cyanides are *just* redissolved, add NaHO in considerable quantity, and then bromine water† until the colour of the bromine persists. Filter.

The **solution** contains sodium cobalticyanide, Na_3CoCy_6.

The cobalt may be confirmed by the borax bead, if the test was not made, or was not satisfactory, with the sulphides.

The **precipitate** consists of the black hydrated sesquioxide of nickel, $Ni_2O_3,3H_2O$.

Confirm (1) by borax bead; (2) wash precipitate, dissolve in HCl, and obtain the characteristic reaction with $(NH_4)_2S$.

* Should the precipitate not be black, only MnS and ZnS can be present; and as these are easily soluble in HCl, the $KClO_3$ should in this case not be added.

† Bromine is more soluble in water containing KBr in solution than in water alone. By the use of such a solution, therefore, unnecessary dilution is avoided.

CHAPTER VII.

THE PHOSPHATES.

THE salts of phosphoric acid, H_3PO_4, are all of them insoluble in water except those of the alkali metals and ammonium. Lithium phosphate is, however, only difficultly soluble. The addition, therefore, of a solution of one of these soluble phosphates to a solution of a metallic salt results in the precipitation of the phosphate of the metal contained in the salt; thus, using hydrogen disodium phosphate as being the most convenient reagent—

$$HNa_2PO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$
$$HNa_2PO_4 + BaCl_2 = HBaPO_4{}^* + 2NaCl$$
$$2HNa_2PO_4 + 3CaCl_2 = Ca_3(PO_4)_2 + 4NaCl + 2HCl$$

The most delicate reaction for the detection of a phosphate is the formation of a canary-yellow crystalline precipitate of *ammonium phosphomolybdate*, upon the addition of a nitric acid solution of ammonium molybdate, $(NH_4)_2MoO_4$, to a solution of a phosphate. A few drops of the solution of a phosphate are taken, and a very large excess of the nitric acid solution of ammonium molybdate is added, and the mixture slightly warmed when the yellow precipitate crystallises out. It is insoluble in water or acid provided a considerable quantity of ammonium molybdate is present. The precipitate is believed to have the composition $12MoO_3,(NH_4)_3PO_4$. It is decomposed by ammonia into $(NH_4)_2MoO_4$ and $(NH_4)_3PO_4$.

When the phosphates, insoluble in water, are acted upon by acids, they either dissolve, or, if the acid employed is capable of forming an insoluble compound with the metal, they are converted into this compound, and phosphoric acid is set free. Thus, calcium phosphate is decomposed by sulphuric acid, insoluble calcium sulphate being formed, while the liberated phosphoric acid passes into solution—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

* It depends upon the conditions of precipitation whether the so-called acid phosphate, $HBaPO_4$, or the normal salt, $Ba_3(PO_4)_2$, is produced.

In those cases where the phosphate is entirely dissolved by the acid, it is reprecipitated unaltered by the addition of ammonia, ammonium sulphide,* caustic alkalies, alkaline carbonates, or in some cases by barium carbonate. For example, the phosphates of Ni, Co, Mn, Zn, Ba, Sr, Ca, and Mg are all soluble in HCl; and if ammonia be added to the hydrochloric acid solution of any one of these, it at once causes the reprecipitation of the phosphate. The significance of this fact, and its bearing upon the method of separation of the metals of Group III., will be obvious. When NH_4Cl and NH_4HO are used to separate Group IIIA. from Group IIIB. by precipitating the hydroxides of Al, Cr, and Fe, they will at the same time throw down the phosphates of all or any of the above-named metals, if they happen to be present as phosphates in the solution under examination. Hence it is necessary to adopt some method for withdrawing the phosphoric acid which is in combination with these metals, and of converting them all into such salts as chlorides before it is possible to attempt their separation on the basis of the plans laid down on pp. 49 and 62.

It will be well, therefore, at this point to enter somewhat fully upon a study of such reactions with phosphates as are made use of in analysis.

The Solution of Phosphates by Acids. I. *By Hydrochloric Acid.*—The phosphates of the metals of Groups III., IV., and V., which are insoluble in water, are dissolved by hydrochloric acid. When such a phosphate is dissolved in this acid, the addition to the solution of any alkali causes the reprecipitation of the phosphate unchanged. This fact is sometimes explained by supposing that the act of solution in these cases, is of the same simple order as the solution of salt in water; that the phosphate dissolves unchanged, being present in the liquid *as a phosphate;* and that, therefore, its reprecipitation by an alkali is simply owing to the removal, by neutralisation, of the solvent acid.

As a matter of fact, however, the process is more complex, for in reality double decomposition between the acid and the phosphate takes place exactly in the same manner as between the calcium phosphate and sulphuric acid given above, except that the metallic salt formed by the union of the metal with the solvent acid is *soluble in water.* Thus, in the case of the solution of barium phosphate in hydrochloric acid—

$$HBaPO_4 + 2HCl = BaCl_2 + H_3PO_4$$

barium chloride and phosphoric acid are formed; and both being

* Except those of Fe, Mn, Ni, Co, Zn. See p. 65.

soluble in water, complete solution results from the action.* $BaCl_2$ and H_3PO_4 are incapable of reacting upon each other, and therefore exist together in the solution.†

Now, when an alkali is added to this solution, it first unites with the phosphoric acid, forming a soluble phosphate of the alkali; this in its turn, by double decomposition with the barium chloride, forms barium phosphate and a chloride of the alkali. The two stages in the reaction may be thus expressed:

$$\left.\begin{matrix}BaCl_2 + H_3PO_4\end{matrix}\right\} + 2NaHO = \begin{cases}(1)\ BaCl_2 + HNa_2PO_4 + 2H_2O \\ (2)\ 2NaCl + HBaPO_4 + 2H_2O\end{cases}$$

In order, therefore, to formulate the various reactions which phosphates in acid solutions undergo, the solution of the phosphate will be expressed in the equations as a mixture of phosphoric acid and the metallic salt of the solvent acid. In this way the mechanism of the reactions will be rendered easy of understanding. Two or three examples of the precipitation of phosphates from hydrochloric acid solutions by various alkaline reagents may be given.

(*a*) Precipitation of calcium phosphate from HCl solution by NH_4HO, giving only the final result—

$$\left.\begin{matrix}3CaCl_2 + 2H_3PO_4\end{matrix}\right\} + 6NH_4HO = 6NH_4Cl + Ca_3(PO_4)_2 + 6H_2O$$

(*b*) Precipitation of aluminium phosphate by $(NH_4)_2S$—

$$\left.\begin{matrix}2AlCl_3 + 2H_3PO_4\end{matrix}\right\} + 3(NH_4)_2S = 6NH_4Cl + 2AlPO_4‡ + 3H_2S$$

In the case of the metals Fe, Mn, Zn, Ni, and Co (metals which are capable of forming insoluble sulphides), the phosphates are not reprecipitated by $(NH_4)_2S$; but the metals are thrown down as sulphides, while the phosphoric acid unites with the ammonia,

* It is quite easy to prove, in this particular case, that when barium phosphate is dissolved in hydrochloric acid, the solution contains barium chloride and phosphoric acid. This may be done by gently evaporating the solution down upon a steam-bath until crystals begin to separate out. If these are drained, and washed a few times with strong hydrochloric acid (in which $BaCl_2$ is nearly insoluble), they can then be dissolved in water. The solution so obtained will be found to give no precipitate with ammonia, therefore showing that it contains no barium phosphate; but it will give all the ordinary reactions for barium.

† Hence it follows that the addition of *phosphoric acid* to such a metallic solution as barium chloride gives no precipitate of barium phosphate.

‡ The simpler formulæ for the phosphates of Al, Cr, and Fe will be used, instead of $Al_2(PO_4)_2$, etc., etc.

and therefore remains in the solution: thus, taking iron as an example—

$$2FeCl_3 + 2H_3PO_4 + 5(NH_4)_2S = 6NH_4Cl + 2FeS + 2H(NH_4)_2PO_4 + 2H_2S + S$$

(*c*) Precipitation of ferric phosphate by $BaCO_3$—

$$2FeCl_3 + 2H_3PO_4 + 3BaCO_3 = 3BaCl_2 + 2FePO_4 + 3CO_2 + 3H_2O$$

In the case of solutions of calcium or magnesium phosphates, the addition of $BaCO_3$ results in the precipitation, not of the calcium or magnesium phosphate, but of barium phosphate; thus—

(*d*) $$3MgCl_2 + 2H_3PO_4 + 3BaCO_3 = 3MgCl_2 + Ba_3(PO_4)_2 + 3CO_2 + 3H_2O$$

II. *By Acetic Acid*, $H(C_2H_3O_2)$.—Of the phosphates of the metals of Groups III., IV., and V., those of aluminium and iron are insoluble in acetic acid, while chromium phosphate is only dissolved with difficulty. The phosphates of the remaining metals of these groups are readily soluble in this acid.

When a phosphate is dissolved in acetic acid, we may, for the same reasons as apply in the case of hydrochloric acid, consider the action as being strictly a chemical one, and may regard the solution as containing the metallic acetate and phosphoric acid; thus, in the case of calcium phosphate—

$$Ca_3(PO_4)_2 + 6H(C_2H_3O_2) = 3Ca(C_2H_3O_2)_2 + 2H_3PO_4{}^*$$

Phosphoric acid, therefore, is incapable of giving a precipitate with a solution of calcium acetate (or the acetate of any metal whose phosphate is soluble in acetic acid). It can, however, precipitate the phosphate from the acetate of a metal whose phosphate is *insoluble* in acetic acid. Thus, if phosphoric acid is added to a solution of aluminium acetate, aluminium phosphate is thrown down, and acetic acid formed—

$$Al(C_2H_3O_2)_3 + H_3PO_4 = AlPO_4 + 3H(C_2H_3O_2)$$

If to a solution of a phosphate (*e.g.* calcium phosphate) in acetic acid, ferric chloride (or aluminium chloride) be added, by double decomposition acetic acid is formed in the solution, and ferric phosphate is therefore precipitated; thus—

$$3Ca(C_2H_3O_2)_2 + 2H_3PO_4 + 2FeCl_3 = 2FePO_4 + 3CaCl_2 + 6H(C_2H_3O_2)$$

* In this solution the presence of the phosphoric acid does not prevent the precipitation of the calcium as calcium oxalate by the addition of ammonium oxalate.

Now, although phosphoric acid is unable to precipitate ferric phosphate when added to ferric chloride (ferric phosphate being soluble in hydrochloric acid), the presence of a soluble acetate, such as sodium acetate, would bring about the same conditions as exist in the above reaction, and therefore again the phosphate of iron will be thrown down—

$$3Na(C_2H_3O_2) + \left.\begin{matrix}\\ H_3PO_4 + FeCl_3\\ \\ \end{matrix}\right\} = FePO_4 + 3NaCl + 3H(C_2H_3O_2)$$

The Removal of Phosphoric Acid.—The phosphoric acid may be separated from a phosphate in two ways : namely, either by causing the *metal* to form some insoluble compound with a reagent, or by making the *phosphoric acid* unite with a reagent to produce an insoluble compound. For example, the phosphoric acid may be withdrawn from the phosphates of iron, manganese, zinc, cobalt, and nickel, by means of ammonium sulphide, as explained on p. 66. In these cases, the metals, in the form of insoluble sulphides, are precipitated, while the phosphoric acid, in combination with ammonia, remains in solution. The disadvantage of this method lies in the fact that the phosphate of ammonia left in the liquid, is able to undergo double decomposition with any other metallic salts which might be present, and precipitate them as phosphates ; therefore the final result would only be that of substituting one insoluble phosphate for another. The following examples will make this clear :—

Suppose a mixture under examination to consist of alumina and phosphate of iron ; on dissolving in hydrochloric acid, we should get the following reaction :—

$$Al_2O_3 + 2FePO_4 + 12HCl = 2AlCl_3 + 2FeCl_3 + 2H_3PO_4 + 3H_2O$$

On adding ammonium sulphide to the solution, the iron is precipitated as FeS and the aluminium as phosphate ; thus—

$$2AlCl_3 + \left.\begin{matrix}\\ 2FeCl_3 + 2H_3PO_4\\ \\ \end{matrix}\right\} + 6(NH_4)_2S = 2FeS + 2AlPO_4 + 12NH_4Cl + 3H_2S + S$$

Or again, if salts of Ba, Sr, Ca, or Mg (other than phosphates) are present with a phosphate which is decomposed by ammonium sulphide, then the ammonium phosphate which is formed would react upon such salts and precipitate the metals as phosphates. Thus, suppose a mixture of zinc phosphate and calcium carbonate is being examined ; as before, it is dissolved in hydrochloric acid, and then, on the addition of ammonium sulphide, a precipitate is

obtained consisting of a mixture of zinc sulphide and calcium phosphate—

$$Zn_3(PO_4)_2 + 3CaCO_3 + 12HCl = 3ZnCl_2 + 2H_3PO_4 + 3CaCl_2 + 3CO_2 + 3H_2O$$

$$3ZnCl_2 + 2H_3PO_4 + 3CaCl_2 + 6(NH_4)_2S = 3ZnS + Ca_3(PO_4)_2 + 12NH_4Cl + 3H_2S + S$$

In the ordinary course of analysis, on the addition of NH_4Cl and NH_4HO for the precipitation of Group IIIA., if phosphates are present they are also precipitated along with the hydroxides of Al, Cr, and Fe. If, therefore, ammonium sulphide be added, any phosphates of Fe, Zn, Mn, Ni, and Co which are present will be converted into sulphides, and the ammonium phosphate which is formed will react upon any compounds of Ba, Sr, Ca, and Mg which might be present, *not as phosphates*, and convert them into phosphates. In analysis, therefore, the second method for removing phosphoric acid is had recourse to, namely, that of employing a reagent which will form an insoluble compound with the *acid*, and so throw it out of solution.

The reagent employed is ferric chloride, and the separation is based upon the fact already explained, viz. that when this salt is added to an acetic acid solution of a phosphate, it precipitates the phosphoric acid as ferric phosphate, leaving the metal, which was originally united to the phosphoric acid, in the solution as a chloride. The separation is made in the following manner :—

Separation of Phosphoric Acid.

The precipitate produced by NH_4HO in presence of NH_4Cl (which may contain the hydroxides of Al, Cr, and Fe, as well as all the phosphates), is dissolved in a little warm dilute HCl, and the solution made *nearly* neutral by the addition of Na_2CO_3.* A mixture of sodium acetate and acetic acid † is then added, and the solution boiled and filtered.‡

* This is in order to remove the *excess* of HCl used in dissolving the precipitate. This acid would, in any case, be neutralised by double decomposition with the sodium acetate, when that reagent is added; but it is better to get rid of it previously by means of sodium carbonate, so that the sodium acetate may be utilised entirely in bringing about the reactions explained on p. 66, and also in the footnote below.

† See list of reagents (Appendix).

‡ If the whole of the phosphoric acid contained in the substance undergoing analysis was originally present in combination with Al, Cr, or Fe, then by this reaction the whole of the phosphoric acid will have been thrown out of

The **precipitate** contains phosphates of Al, Cr, or Fe.

This precipitate may be treated with Na_2O_2 exactly as the hydroxides, p. 49. $AlPO_4$ dissolves in the NaHO, and $CrPO_4$ is oxidised into Na_2CrO_4. On filtering, the iron is left on the filter. The Al may be detected by neutralisation and reprecipitation with NH_4HO. The chromium by $BaCl_2$ in acetic acid solution. (Barium phosphate is not precipitated in presence of acetic acid.)

The **filtrate.** $FeCl_3$ is added drop by drop * until precipitation is complete, at which point the liquid will begin to assume a distinct reddish colour (due to the formation of soluble ferric acetate).† The mixture is gently boiled for a few minutes (whereby the ferric acetate is converted into an insoluble basic acetate), and then filtered.

The precipitate, containing the whole of the phosphoric acid as ferric phosphate and more or less basic ferric acetate, is thrown away. The solution now contains the metals of Groups IIIB. and IV., as well as Mg, in the form of chlorides. Their separation is made by the usual methods.

solution. Moreover, even if some of the phosphoric acid had been originally present in combination with other metals, it might happen that there was also present enough aluminium or iron, *not as phosphate*, to combine with all the phosphoric acid of these other phosphates, and so to cause the complete removal of this acid. The following example will make this clear: Suppose a mixture of aluminium phosphate, ferric oxide, and calcium phosphate is to be examined. When this has been dissolved in HCl, we may represent the action of sodium acetate in the following manner:—

$$\left.\begin{array}{l} AlCl_3 + H_3PO_4 \\ +\,2FeCl_3 \\ +\,3CaCl_2 + 2H_3PO_4 \\ +\,9Na(C_2H_3O_2) \end{array}\right\} = \begin{cases} AlPO_4 + 2FePO_4 & \text{precipitated} \\ 3NaCl + 3H(C_2H_3O_2) + 6NaCl + 6H(C_2H_3O_2) + 3CaCl_2 & \text{in solution} \end{cases}$$

If more than enough ferric chloride is present than is required to take the whole of the phosphoric acid from the calcium phosphate (or other similar phosphates), then *all* the phosphoric acid is thrown down, and the excess of the $FeCl_3$ passes into the solution. But if, on the other hand, there is an excess of calcium phosphate, it passes into solution owing to the free acetic acid present. If no compounds of Al, Cr, or Fe are present, either as phosphates or otherwise, no precipitate will be produced by the sodium acetate.

* If the first drops of $FeCl_3$ produce no precipitate, it proves that all the phosphoric acid has already been thrown down (see previous note). The metals are all present, therefore, as chlorides, and their separation may be made by the ordinary methods.

† Ferric acetate is formed by the action of the excess of ferric chloride upon the sodium acetate present; thus—

$$FeCl_3 + 3Na(C_2H_3O_2) = Fe(C_2H_3O_2)_3 + 3NaCl$$

It is very important to avoid the use of any unnecessary excess of $FeCl_3$, for the precipitated ferric phosphate is soluble both in ferric chloride and in ferric

APPENDIX TO CHAPTER VII.

THE RARE METALS OF GROUP III.*

These elements may for convenience be arranged in five groups, based upon the composition of the precipitates which are thrown down by the group-reagents :

(1)	(2)	(3)	(4)	(5)
Beryllium	Scandium Yttrium Ytterbium Cerium Lanthanum	Zirconium Thorium	Titanium Tantalum Niobium	Uranium Indium (Thallium) † Vanadium ‡

Those of the first three divisions are precipitated in the form of hydroxides, which are *basic* in their character. Those of the fourth division are thrown down in the form of hydrated oxides of a more or less *acidic* character, while the remaining metals come down as sulphides. The composition of the various compounds is as follows :—

(1)	(2)	(3)	(4)	(5)
$Be(HO)_2$	$Sc(HO)_3$ $Y(HO)_3$ $Yb(HO)_3$ $Ce(HO)_3$ $La(HO)_3$	$Zr(HO)_4$ $Th(HO)_4$	H_2TiO_3 H_2TaO_4 H_3NbO_4	$(UO_2)S$ InS $(Tl_2S)^2$

Beryllium.—Named from *beryl*, the chief source of the element. The sulphate, $BeSO_4$, is the most readily obtained salt.

The reactions of this element resemble very closely those of aluminium—so much so, that at one time the two elements were

acetate. The transformation of soluble ferric acetate into the insoluble basic acetate by boiling, is expressed as follows :—

$$3Fe(C_2H_3O_2)_3 + 3H_2O = Fe(C_2H_3O_2)_3,Fe_2O_3 + 6H(C_2H_3O_2)$$

In cases where very small quantities of a phosphate and a great excess of iron are present in the substance under examination, it is necessary to reduce the iron to the "ferrous" state by means of sulphurous acid. Ferrous salts do not dissolve ferric phosphate.

* A systematic study of the reactions of the rare metals lies entirely outside the scope of this book. In many cases it is almost impossible to purchase the compounds in anything approaching to a condition of purity, while with most of the metals the cost of the salts practically prohibits such a course (see note, p. 26). These elements, however, are not all equally "rare," and therefore in this section some of the characteristic reactions of a few of the most commonly occurring of these metals are given.

† Thallium also appears in Group I. (see p. 16), since the chloride is precipitated by hydrochloric acid from *thallous* solutions; and, like lead chloride, is slightly soluble in water.

‡ See footnote on p. 18.

regarded as belonging to the same natural family. Thus, ammonia, potash, and soda produce, with solutions of either metal, a white flocculent precipitate of the respective hydroxides, $Al_2(HO)_6$ and $Be(HO)_2$.

Both precipitates are soluble in excess of the fixed alkalies, but the beryllium compound is reprecipitated if the diluted solution is boiled.

Beryllium hydroxide is decomposed by boiling with ammonium chloride, ammonia being evolved and beryllium chloride passing into solution; thus—

$$Be(HO)_2 + 2NH_4Cl = BeCl_2 + 2NH_3 + 2H_2O$$

Aluminium hydroxide undergoes no change when similarly treated, hence the metals may be separated by this reaction.

The carbonates of the alkalies give precipitates of beryllium carbonate, or basic carbonate; readily soluble in excess of ammonium carbonate, giving a double carbonate.

The precipitate is soluble, but far less readily, in the carbonates of the fixed alkalies. Beryllium is therefore readily separated from aluminium by adding ammonium carbonate and warming the solution. Aluminium hydroxide is precipitated, while the beryllium goes into solution as the double carbonate of ammonium and beryllium. On filtering off the aluminium hydroxide, the beryllium hydroxide may be precipitated by ammonia, after first neutralising with hydrochloric acid.

The salts of beryllium possess a characteristic sweet taste, hence the name *glucinum*, which was formerly applied to the element.

Zirconium.—The oxide of this element, along with others of the so-called "rare earths" (but more especially *Zirconia*), has the property of remaining unchanged for a long time when heated to incandescence, and of emitting a bright white light when so heated. It is on this account used, with others of the rare earths, in the construction of the "mantles" of the incandescent gas-burners now so common.

Alkaline hydroxides, as well as ammonium sulphide (group-reagent), give a white precipitate of zirconium hydroxide, $Zr(HO)_4$, resembling aluminium hydroxide in appearance. It is distinguished from the latter in that it is insoluble in excess of potassium or sodium hydroxide.

Alkaline carbonates give a white precipitate consisting of a basic carbonate, which is soluble in excess, especially of ammonium carbonate.

Potassium sulphate (a concentrated boiling solution) gives a precipitate of a double sulphate, which, when thrown down from the hot solution, is scarcely soluble in hydrochloric acid (thorium gives a similar precipitate under the same conditions, but the thorium compound is soluble in hydrochloric acid). In dilute solutions the precipitate only appears after standing for some hours. Sodium thiosulphate gives a precipitate of zirconium thiosulphate,

which on boiling is complete even in very dilute solutions (thorium behaves similarly). Oxalic acid gives a white precipitate of zirconium oxalate, soluble in ammonium oxalate. (Thorium oxalate, similarly precipitated, is *insoluble* in ammonium oxalate.)

Hydrogen peroxide, added to a slightly acid solution of a zirconium salt, gives a white precipitate, believed to be either ZrO_3 or Zr_2O_5. (Niobium and titanium do not give a precipitate.)

By means of these three reactions zirconium can be separated from the other "rare earths" of this group.

The hydrated oxides, which are precipitated by ammonia, are first dissolved in hydrochloric acid, and the solution nearly neutralised with sodium carbonate. Sodium thiosulphate is then added, and the mixture boiled. The precipitate may consist of the thiosulphates of zirconium and thorium, together with titanic acid. The precipitate is treated with boiling hydrochloric acid, which dissolves the two thiosulphates, and possibly a little titanic acid. Excess of ammonium oxalate is added to the solution, which at first precipitates oxalates of zirconium and thorium, but redissolves the zirconium oxalate. The insoluble thorium oxalate is removed by filtration, and any titanium in the solution is precipitated by means of ammonium carbonate, added in excess in order to redissolve the zirconium basic salt, which is first thrown down. Any permanent precipitate is filtered off, and the filtrate concentrated by gentle evaporation. A boiling strong solution of potassium sulphate is then added, which precipitates the double sulphate of potassium and zirconium.*

Titanium.—This element is met with in small quantities in many specimens of iron ores, clays, and igneous rocks. The minerals special to the element, *rutile*, *anatase* (TiO_2); *sphene* (silicate and titanate of calcium), are rare substances—*titaniferous iron* (ferrous titanate) is less rare.

Titanium oxide, TiO_2, being insoluble in hydrochloric and nitric acid, is found in the insoluble residue after treatment with acids; titanates, on the other hand, are dissolved by hydrochloric acid, but on boiling the solution white titanic acid, H_2TiO_3, is precipitated.

Titanium oxide (in the absence of other metals which colour a bead of microcosmic salt), when heated in a bead of microcosmic salt in the *inner* blowpipe flame, imparts to the bead a colour which is yellowish when hot, but which becomes violet as the bead

* This separation, and the reactions for zirconium, may be made by dissolving up a couple of the incandescent gas "mantles;" either new ones, or those which have become worn out by use. In the former case they should first be set fire to, in order to burn off the organic matter present. The mantles are boiled in a test-tube with a little strong sulphuric acid, and the liquid when cold diluted with water. The insoluble residue (consisting of the main portion of the material) is filtered off, and the hydrated oxides of the rare earths, along with any alumina, are precipitated by the addition of ammonia. The precipitate is then washed, and dissolved in a small quantity of hydrochloric acid.

cools. The colour is more readily obtained by the aid of some additional reducing agent besides the reducing flame; thus if the salt be heated on charcoal instead of a platinum wire, or if a trace of zinc be added, the result is more quickly obtained. In the presence of small quantities of iron the bead appears brown-red.

Titanium dioxide is separated from silicon dioxide (or silicates) by the action of hydrofluoric acid (sulphuric acid being present to prevent the volatilisation of titanium, as fluoride). Titanium is obtained in solution (and separated from silica, and also from compounds of tantalum and niobium) by fusion with hydrogen potassium sulphate. The "melt" is extracted with cold water, when the titanium passes into solution as a sulphate.

When titanium oxide is fused with potassium carbonate, potassium titanate, K_2TiO_3, is formed, which, being insoluble in water, may be separated from any alkaline silicate by extracting the melt in *cold* water.

If the residue of potassium titanate be then treated with cold dilute hydrochloric acid, it dissolves, the solution containing titanic acid, $Ti(HO)_4$ or $TiO_2,2H_2O$. If this solution be heated, the titanic acid is rendered insoluble, and is therefore precipitated, the precipitate being the hydrated oxide H_2TiO_3, or $TiO(HO)_2$, or TiO_2,H_2O.

If to the cold solution of titanic acid there be added ammonia, or the hydroxide or carbonate of the alkalies, or ammonium sulphide, a white precipitate is produced, consisting of the hydrated compound $Ti(HO)_4$, or $TiO_2,2H_2O$, which redissolves readily in dilute hydrochloric acid or sulphuric acid. Moderate rise of temperature at once converts this soluble compound into the insoluble titanic acid, H_2TiO_3, or TiO_2,H_2O.

Uranium.—Like the element chromium, uranium forms uran*ous* and uran*ic* salts, as well as uran*ates*.

The uranous salts are derived from uranous oxide, UO_2, in which the element is tetravalent. Thus, uranous sulphate is represented by the formula $U(SO_4)_2$.

These salts readily pass by oxidation into uranic compounds, and are therefore powerful reducing agents. They are for the most part green in colour. The uranic or *uranyl* salts are derived from the oxide, UO_3, or $(UO_2)O$, in which the element is hexavalent. They are regarded as containing the divalent radical uranyl, (UO_2), which takes the place of a divalent metal; thus, uranyl sulphate and nitrate are expressed by the formulæ $(UO_2)SO_4,3H_2O$ and $(UO_2)(NO_3)_2,6H_2O$ respectively. These salts are mostly yellow in colour, and soluble in water.

The uranates are constituted like the dichromates (uranates corresponding to normal chromates are not known). Thus, sodium uranate, $Na_2U_2O_7$, analogous to sodium dichromate, $Na_2Cr_2O_7$.

Uranyl nitrate and acetate are the salts most commonly met with, being used in the volumetric determination of phosphoric acid.

Alkaline carbonates give with *uranyl* salts a yellow precipitate,

consisting of a double carbonate of uranium and the alkali. The precipitate is soluble in excess of the reagent.

The uranium in this solution is not precipitated by ammonium sulphide. If the solution be neutralised with acid, a uranate of the alkali is thrown down.

With *uranous* salts, these reagents give a green precipitate, also soluble in excess.

Caustic alkalies give with *uranyl* salts a yellow precipitate of the uranate of the alkali, insoluble in excess of the reagent.

With *uranous* salts, these reagents give a chocolate-coloured precipitate of uranous hydroxide, $U(HO)_4$.

Ammonium sulphide gives with *uranyl* salts a brown precipitate of uranyl sulphide, $(UO_2)S$, insoluble in excess of the reagent, but soluble in normal ammonium carbonate.

In acid solutions sulphuretted hydrogen reduces *uranyl* to *uranous* compounds.

Potassium ferrocyanide gives with *uranyl* salts a brown precipitate. This reagent is employed as an *indicator* in the volumetric estimation of phosphoric acid by means of uranyl salts.

CHAPTER VIII.

The Metals of Group II.

The metals of this group (as well as those of Group I.) are characterised by their common property of forming sulphides in an acid solution ; that is to say, their sulphides are insoluble in dilute acids. By this property they are all sharply separated from the metals of Group III. The acid which has been found to be the most convenient to have present, is hydrochloric acid ; and since, on acidifying with this acid preparatory to the precipitation of the sulphides, the *chlorides* of silver, lead, and *mercurous* mercury * are

* Mercury forms two classes of salts, *mercuric* and *mercurous;* and the relation in which they stand to each other is very interesting. In the compounds of the first type, the metal is playing the part of an ordinary divalent element, replacing two atoms of hydrogen in acids and giving such salts as $HgCl_2$, $Hg(NO_3)_2$, $HgSO_4$, HgS, etc. In the mercurous compounds the proportion of mercury to the negative radical is twice as great as in the mercuric salts, hence the composition of, say, mercurous chloride may be expressed either by the formula Hg_2Cl_2 or HgCl. Some chemists adopt the latter formula, and, regarding the mercury in *mercurous* compounds as acting the part of a monovalent element, express the various salts by such formulæ as $HgNO_3$, Hg_2SO_4, etc. Others prefer to consider the mercurous salts as compounds, in which the divalent radical, or double atom, (Hg_2), is substituted for the single divalent atom, (Hg), and therefore express the compounds by such formulæ as Hg_2Cl_2, $Hg_2(NO_3)_2$, Hg_2SO_4. The density of the vapour yielded by heating mercurous chloride is 117·59, which, being half that demanded by the formula Hg_2Cl_2, gave support to the view that HgCl was the correct formula. But it has since been shown that the compound dissociates on heating, into mercuric chloride, $HgCl_2$, and Hg (mercury giving monatomic molecules). In the absence of any conclusive evidence in favour of either view, the formulæ adopted for mercurous compounds in this book will be those which represent them as containing the double atom (Hg_2). As the two classes of compounds present great differences in their chemical reactions, behaving, indeed, more like compounds of two different metals, one of which belongs to Group I. and the other to Group II., there is at least some advantage in employing a symbol for *mercurous* mercury (Hg_2), which at a glance distinguishes it from that used to denote *mercuric* mercury, Hg. All the salts of mercury will therefore be formulated as salts of a dibasic metallic radical, which in the *mercuric* compounds has the symbol Hg, and in the *mercurous* salts (Hg_2) (with or without the bracket). Thus—

Chlorides, $HgCl_2$	...	...	...	...	$(Hg_2)Cl_2$
Sulphates, $HgSO_4$	...	...	...	...	$(Hg_2)SO_4$

thrown down, these three metals are treated separately, and constitute Group I.

The precipitation of these three metals as chlorides, however, is only *complete* in the case of Ag and (Hg_2). Lead chloride is soluble to some extent even in cold water, hence a portion of the lead passes through into Group II.

The metals of Group II. are divided into two sections, namely—

(1) Metals whose sulphides are insoluble in ammonium sulphide—

Mercury (*mercuric*), **lead, bismuth, cadmium, copper.**

(2) Metals whose sulphides dissolve in ammonium sulphide—

Arsenic, antimony, tin, gold, platinum.

REACTIONS OF THE METALS OF GROUP II.—DIVISION 1.

Mercury, Hg.

DRY REACTIONS.—When heated alone in a tube, many mercury compounds (those with the halogens, for example) volatilise unchanged, giving sublimates of the same compound. The iodide (red) when heated forms a sublimate, consisting chiefly of the yellow allotropic form of HgI_2, which when cold changes to red if scratched or rubbed. Some mercury compounds when heated decompose, and metallic mercury volatilises and sublimes in the tube.

If a mercury salt be mixed with several times its weight of sodium carbonate (both being as dry as possible), and the mixture be strongly heated in a dry narrow test-tube, a sublimate of metallic mercury will be obtained. The sublimed mercury will present the appearance of a bright metallic mirror, but if examined by means of a lens, or if rubbed with a glass rod, distinct globules of liquid metal will be visible.

WET REACTIONS.—(*a*) **Mercuric Compounds.**—Of the common salts, the nitrate, sulphate, chloride, and bromide (*but not the iodide*) are soluble in water, but the solubility is not very great.

KHO or NaHO gives with mercuric compounds a yellow precipitate * of mercuric oxide, HgO—

$$HgCl_2 + 2KHO = HgO + H_2O + 2KCl$$

Nitrates, $Hg(NO_3)_2$	$(Hg_2)(NO_3)_2$
Basic nitrates, $Hg(NO_3)_2,2HgO,H_2O$ ...	$(Hg_2)(NO_3)_2,(Hg_2)O,H_2O$
Double ammonium compounds, NH_2HgCl	$NH_2(Hg_2)Cl$

* On the first addition of the reagent, the precipitate appears a brownish colour (probably due to the momentary formation of the hydroxide, which is incapable of existing), but almost immediately it becomes yellow. Why the oxide obtained by precipitation should be yellow, while that prepared in the dry way is brick-red, is not known. Compare also the sulphide.

The precipitate is insoluble in excess of the reagent.

NH_4HO produces a white precipitate of an ammoniacal mercuric compound, where two atoms of hydrogen from the ammonium radical are replaced by the divalent atom Hg; thus—

$$HgCl_2 + 2NH_4HO = NH_2HgCl + NH_4Cl + 2H_2O$$

Or with mercuric nitrate—

$$Hg(NO_3)_2 + 2NH_4HO = (NH_2Hg)NO_3 + NH_4NO_3 + 2H_2O$$

H_2S produces a black* precipitate of HgS. The precipitation is only complete after some time, and when the solution is considerably dilute. The compound is insoluble in HCl, and in HNO_3 even when boiling. (The prolonged action of boiling HNO_3 partially converts it into the white compound $Hg(NO_3)_2$, 2HgS.) Mercuric sulphide dissolves in *aqua regia*, forming mercuric chloride. In the presence of caustic alkalies it dissolves in sodium or potassium sulphide (*not in ammonium sulphide*), forming the double sulphides, HgS,Na_2S and HgS,K_2S.

$(NH_4)_2S$ gives the same precipitate. The same result is also obtained by the addition of sodium thiosulphate, $Na_2S_2O_3$, to a warm solution acidified with HCl.

KI precipitates HgI_2 as a rich scarlet compound, soluble in excess of either solution. When first precipitated it appears yellow, but quickly turns salmon-red and then scarlet. The compound is dimorphous, and can be obtained either in the red (*quadratic crystals*) or the yellow (*rhombic prisms*) variety.

Reduction of Mercuric Compounds.—By reducing agents mercuric compounds may be converted into mercurous salts, or the reduction may go a stage further and result in the precipitation of mercury in the metallic state. Thus, on the addition of stannous

* The progress of this precipitation is accompanied by very characteristic changes of colour. The first action of the H_2S is to give a *white* precipitate, which then passes through various shades of colour, from yellow to yellowish-red, to brown, and lastly, black. The white substance is a compound of HgS with the mercuric salt in solution, $HgCl_2$,2HgS, or $Hg(NO_3)_2$,2HgS, and the changes in colour are ascribed to the gradual conversion of this into black, HgS. It does not appear quite obvious, however, how a gradual alteration in the proportions of the *white* double compound and the *black* sulphide can give the orange and reddish tints which are seen. Mercuric sulphide prepared by other processes is red (the pigment known as *vermilion*). Why the compounds prepared in different ways should be so very different in colour is not known; probably it is a case of dimorphism similar to that exhibited by HgI_2, and it may be that to some extent the *red* HgS is precipitated, but is not stable under the conditions which are present, and so passes into the black modification.

chloride, $SnCl_2$, a white precipitate of mercurous chloride is produced—

$$2HgCl_2 + SnCl_2 = (Hg_2)Cl_2 + SnCl_4$$

On gently warming with an excess of stannous chloride, the precipitated mercurous chloride changes to a grey deposit of mercury in a condition of fine powder—

$$(Hg)_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg$$

Many metals are capable of displacing mercury from its solutions, the mercury being deposited upon the metal. Thus, if a strip of clean copper be immersed in a neutral or slightly acid solution of a mercury salt, it becomes coated with a white silvery deposit of an amalgam of copper and mercury, from which the mercury can be readily volatilised and obtained as a metallic sublimate by heating the copper in a dry test-tube. In the case of mercuric salts, the action may be regarded as taking place in two stages; thus—

$$2Hg(NO_3)_2 + Cu = (Hg_2)(NO_3)_2 + Cu(NO_3)_2$$
$$(Hg_2)(NO_3)_2 + Cu = 2Hg + Cu(NO_3)_2$$

(*b*) **Mercurous Compounds.**—Of the common salts mercurous nitrate is the only one which is readily soluble, and this only so long as the water is acid with nitric acid. The addition of much water results in the precipitation of a basic nitrate. Mercurous sulphate is soluble with difficulty.

KHO or NaHO throws down a black precipitate of $(Hg_2)O$. Mercurous oxide is very unstable. When gently warmed, or even upon exposure to light, it is converted into HgO and Hg.

NH_4HO precipitates an ammoniacal mercurous compound, which is black. Its composition is exactly analogous to the corresponding mercuric compound—

$$Hg_2(NO_3)_2 + 2NH_4HO = NH_2(Hg_2)NO_3 + NH_4NO_3$$

H_2S produces a black precipitate, which is a mixture of HgS and Hg. (Hg_2S is not known to exist.) This precipitate, therefore, behaves, on treatment with nitric acid, in the same way as that obtained from a *mercuric* solution. If we imagine the free atom of mercury as first dissolving in the acid, the mercuric nitrate so formed unites with HgS, giving the white insoluble compound $Hg(NO_3)_2{}_2HgS$.

$(NH_4)_2S$ gives the same precipitate, but in this case the free mercury will be also converted into HgS in proportion as the ammonium sulphide contains more or less polysulphide, for alkaline polysulphides convert metallic mercury into HgS.

HCl and soluble chlorides precipitate white mercurous chloride, Hg_2Cl_2. Insoluble in dilute acids ; soluble in boiling HNO_3, being converted into $HgCl_2$ and Hg, and the mercury then dissolves to mercuric nitrate, with evolution of oxides of nitrogen.

Long boiling with concentrated HCl decomposes Hg_2Cl_2 into $HgCl_2$ (which dissolves) and Hg, which separates (mercury being insoluble in HCl). Chlorine water converts it into mercuric chloride ; thus—

$$Hg_2Cl_2 + Cl_2 = 2HgCl_2$$

Ammonia converts it into *black* mercurous ammonium chloride, $NH_2(Hg_2)Cl$. (This constitutes one of the most characteristic reactions for mercurous compounds.)

Mercurous salts are reduced to metallic mercury by the reducing agents which reduce the mercuric compounds ; thus, with stannous chloride a grey precipitate of mercury is at once produced—

$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl = SnCl_4 = 2HNO_3 + 2\,Hg$$

Lead, Pb.

Dry Reactions.—Lead compounds are very readily reduced when heated upon charcoal before the blowpipe flame, either alone or mixed with sodium carbonate or potassium cyanide. Globules of metallic lead are thus obtained, and at the same time a yellowish incrustation is formed, consisting of the oxide, PbO (*litharge*). When cold, one of the globules can be removed and the properties of the metal examined. Lead may be recognised by its malleability and softness, the latter property enabling it to leave a black mark when rubbed upon paper. It is insoluble in cold HCl or H_2SO_4, but readily dissolves in HNO_3, forming $Pb(NO_3)_2$, which, being insoluble in nitric acid, remains as a white deposit, but which dissolves on dilution with water.

Wet Reactions.—The only salts of lead which are met with in analysis are derived from plumbic oxide, PbO, in which the metal is divalent.* Of the common salts, the nitrate and acetate are readily soluble in water ; the chloride, bromide, and iodide are sparingly soluble.

KHO, NaHO, or NH_4HO gives a white precipitate of either lead hydroxide or a basic compound, depending upon whether the lead solution or the alkali is in excess all the time. For example, if the potash be added to the lead solution, the precipitation

* Salts are known in which lead is tetravalent, *e.g.* lead tetracetate, $Pb(C_2H_3O_2)_4$. The compound $PbCl_4$ has also been obtained.

In the case of bismuth chloride, the oxychloride is thrown down—

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

This compound is not so easily dissolved by HCl as the basic nitrate is by HNO_3, therefore the reaction is complete, the whole of the bismuth being precipitated if the solution is dilute.

KHO, NaHO, or NH_4HO precipitates the white hydroxide $Bi(HO)_3$, or $Bi_2O_3,3H_2O$.* Insoluble in excess of the precipitants. From boiling solutions, or on heating to boiling, the monohydrated oxide is formed, Bi_2O_3,H_2O.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ throws down a white basic carbonate, $(BiO)_2CO_3$.† Insoluble in excess of the reagents.

H_2S or $(NH_4)_2S$ precipitates bismuthous sulphide, Bi_2S_3, as a dark brown, almost black, compound. Soluble in HNO_3; insoluble in alkaline sulphides.‡

Sulphuric acid produces no precipitate with a bismuth salt. Potassium dichromate, $K_2Cr_2O_7$, precipitates basic bismuth dichromate, $(BiO)_2Cr_2O_7$. *Insoluble in* KHO. (These two reactions distinguish between Pb and Bi.)

The most characteristic reaction for bismuth is the formation of the insoluble oxychloride, BiOCl, on the addition of water to an acid solution of $BiCl_3$. As explained above, the reaction with the chloride is more delicate than with the nitrate, hence, if the nitrate is used, it should be converted into the oxychloride. This can be accomplished by the addition of sodium chloride, whereby both the precipitated basic nitrate, as well as the normal nitrate remaining dissolved, are converted by double decomposition into oxychloride; thus—

$$Bi(NO_3)_3,2Bi(HO)_3 + 3NaCl = 3BiOCl + 3H_2O + 3NaNO_3$$
$$\text{or, } Bi(HO)_2NO_3 + NaCl = BiOCl + H_2O + NaNO_3$$
$$Bi(NO_3)_3 + 3NaCl + H_2O = BiOCl + 3NaNO_3 + 2HCl$$

as a molecule of bismuth nitrate, in which two of the NO_3 groups are replaced by (HO); thus, $Bi(HO)_2NO_3$. The composition in both cases is the same, the simpler formula being merely the other divided by three.

* Three hydrated oxides are known, $Bi_2O_3,3H_2O$, $Bi_2O_3,2H_2O$, and Bi_2O_3,H_2O.

† Or this may be regarded as normal bismuth carbonate and oxide, $Bi_2(CO_3)_3,2Bi_2O_3$.

‡ In this respect bismuth differs from the elements Sb and As, with which it is associated in the "natural" or periodic classification. These two elements form soluble thioantimonates and thioarsenates, no such compounds of bismuth being known.

Cadmium, Cd.

DRY REACTIONS.—Cadmium compounds, heated on charcoal with sodium carbonate, are easily reduced ; but, owing to the ready volatility of the metal, the latter is converted into the oxide, which is deposited as a brown incrustation upon the charcoal.*

WET REACTIONS.—The metal strongly resembles zinc (with which it is associated in the natural classification) in its behaviour towards acids, dissolving readily in dilute acids with evolution of hydrogen, or, in the case of nitric acid, of oxides of nitrogen. Only one series of salts is known, derived from the only oxide, CdO. Of the common salts, the nitrate, sulphate, chloride (bromide, iodide, and acetate) are soluble in water.

KHO, NaHO, or NH_4HO precipitates the white hydroxide, $Cd(HO)_2$. Insoluble in excess of KHO or NaHO, but soluble in NH_4HO.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ gives a white precipitate of $CdCO_3$. The presence of NH_4HO prevents the precipitation. The precipitate is not soluble in excess of the reagent as ordinarily used ; but it dissolves in concentrated solutions of K_2CO_3 and Na_2CO_3. From this solution it is reprecipitated on dilution.

H_2S or $(NH_4)_2S$ precipitates cadmium sulphide, CdS, distinguished from the sulphides of all the other metals of this division by its pure yellow colour. It is more easily soluble in acids than the other sulphides of the group, and therefore the acid solution from which it is precipitated must be dilute, and not too strongly acid, to ensure complete precipitation.

CdS is insoluble in potassium cyanide, therefore it is capable of being precipitated in the presence of this salt. And for the same reason, H_2S will throw down a precipitate of CdS from a solution of $CdCy_2$ in excess of KCy, which contains the double cyanide $CdCy_2,2KCy$ (see Method of Separation from Copper). CdS is insoluble in alkaline sulphides, which distinguishes it from arsenious sulphide, which is the only other yellow sulphide (see footnote, p. 77).

Copper, Cu.

DRY REACTIONS.—Copper compounds are reduced to metallic copper when strongly heated upon charcoal along with sodium

* With the exception of the rare mineral *greenockite*, CdS, cadmium is always found in nature closely associated with zinc ores, and only in small quantities. Being much more volatile, however, than zinc, it is often possible to obtain the brown incrustation of CdO before enough of the zinc has been vaporised to mask the reaction.

carbonate in the reducing flame. Reddish scales, or even globules, of metal will be found. Heated in a borax bead, copper salts impart a colour which is green while the bead is hot, but bluish when cold. A more delicate dry test for copper is made by heating the compound upon a platinum loop in a Bunsen flame, and supplying the flame at the same time with a little hydrochloric acid gas, which is admitted by one of the air-holes of the lamp. A little strong hydrochloric acid is heated in a test-tube having a delivery tube leading into one of the air-holes, in the manner shown in Fig. 11. Under these circumstances, the copper compound, which

Fig. 11.

may otherwise impart no colour to the flame, gives a brilliant blue colour, which instantly changes to green when the supply of acid gas is momentarily stopped by partially withdrawing the test-tube.

Wet Reactions.—Copper is not acted upon by dilute HCl or dilute H_2SO_4. Boiling strong HCl slowly dissolves it, giving cuprous chloride and hydrogen. Hot concentrated H_2SO_4 gives SO_2 and copper sulphate. Nitric acid readily dissolves the metal, forming $Cu(NO_3)_2$ and oxides of nitrogen. Copper forms two series of salts, *cuprous* and *cupric*, derived from the two oxides Cu_2O and CuO. The former readily pass by oxidation into cupric compounds.

(*a*) **Cupric Salts.**—Of the common *cupric* salts, the sulphate, nitrate, chloride (bromide and acetate) are readily soluble in water. In the crystallised or hydrated condition they are blue or green, but in the anhydrous state either white or pale yellow.

KHO or NaHO produces a pale blue precipitate of cupric hydroxide or hydrated oxide $Cu(HO)_2$ or CuO,H_2O. Insoluble in excess.* On warming the mixture (or if the precipitation is conducted with hot solutions), this loses a portion of its water of hydration and is changed to a nearly black hydrated oxide—

$$3CuO,H_2O \text{ or } Cu(HO)_2,2CuO$$

NH_4HO or $(NH_4)_2CO_3$ precipitates a light blue basic compound, readily soluble in excess to a deep blue solution (characteristic of copper compounds). If the blue solution be allowed to evaporate, it deposits dark blue crystals, having the composition $CuSO_4,4NH_3,H_2O$ † in the case of the sulphate; and $CuCl_2,4NH_3,H_2O$ with the chloride.

K_2CO_3 or Na_2CO_3 gives a greenish precipitate of the basic carbonate, $Cu(CO_3),Cu(HO)_2$.‡ Insoluble in excess of the reagent under ordinary circumstances. If, however, the reagent be a highly concentrated solution of the alkaline carbonate, the precipitate dissolves to a deep blue solution, believed to contain a double carbonate of copper and the alkali. Dilution with water decomposes this compound, and reprecipitates the basic carbonate (see also Cd, Ni, Co, Fe). On boiling the mixture, the precipitate is converted into the black hydrated oxide; thus—

$$3[CuCO_3,Cu(HO)_2] = 2[Cu(HO)_2,2CuO] + 3CO_2 + H_2O$$

H_2S or $(NH_4)_2S$ produces a nearly black precipitate of cupric sulphide, CuS,§ which, when exposed to the air in a moist condition, absorbs oxygen and is converted into the sulphate. *The precipitate is slightly soluble in ammonium sulphide.* It readily dissolves in potassium cyanide, therefore H_2S fails to give a precipitate of copper sulphide from a solution of Cu_2Cy_2 ‖ in KCy (which contains cuprous potassium cyanide, $Cu_2Cy_2,6KCy$) (compare cadmium).

* In the presence of tartaric acid (or alkaline tartrates), $Cu(HO)_2$ is dissolved by excess of KHO (Fehling's solution. See below).

† Copper sulphate crystals themselves have the composition $CuSO_4,5H_2O$.

‡ This compound occurs in nature as the mineral *malachite*.

§ The composition of precipitated cupric sulphide is said to be represented by the formula Cu_4S_3 (Thomson).

‖ See cuprous cyanide.

Reduction of Cupric Salts.—(1) Many organic substances reduce cupric salts in alkaline solutions, with precipitation of cuprous oxide, Cu_2O. Thus, if KHO be added to a solution of $CuSO_4$ in the presence of grape sugar, the $Cu(HO)_2$ first precipitated dissolves in excess of KHO, giving a blue solution; on gently warming the liquid, a bright red precipitate of Cu_2O is thrown down.* The reaction may be regarded as an abstraction of one atom of oxygen, by the sugar, from two molecules of cupric oxide—

$$2CuO = Cu_2O + O$$

Cuprous oxide is soluble in hydrochloric acid, with the formation of cuprous chloride.

(2) Cupric salts may be reduced by nascent hydrogen. Thus, when metallic copper is placed in a solution of cupric chloride in strong hydrochloric acid, and the mixture boiled, the green cupric chloride becomes colourless, owing to its conversion into cuprous chloride by the hydrogen disengaged by the action of the HCl upon the copper—

$$2CuCl_2 + H_2 = Cu_2Cl_2\dagger + 2HCl$$

If the colourless solution be poured into water, the cuprous chloride is thrown down as a white precipitate; insoluble in water, soluble in HCl, in NH_4HO, and in NH_4Cl.

(*b*) **Cuprous Salts.**—The common cuprous salts are all insoluble in water. For the reactions, a solution of cuprous chloride in hydrochloric acid may be used.

KHO or NaHO gives a yellow precipitate of cuprous hydroxide, $Cu_2(HO)_2$ or Cu_2O,H_2O. If the mixture be heated, the precipitate is converted into the red cuprous oxide.

NH_4HO gives no precipitate, but forms a soluble compound having the composition $Cu_2Cl_2,2NH_3$. The solution is colourless, but has the property (also possessed by the solution of Cu_2Cl_2 in HCl) of absorbing oxygen from the air, first becoming brown, and finally depositing a greenish precipitate of cupric oxychloride, $CuCl_2,3CuO,4H_2O$.‡

* This reaction is utilised as a test for sugar. The reaction is more delicate when an alkaline solution of cupric tartrate (Fehling's solution) is employed. This is prepared by neutralising a solution of tartaric acid with excess of KHO, and adding to the alkaline liquid a small quantity of copper sulphate solution. A light blue solution is obtained.

† The *cuprous* and *cupric* compounds are related to each other in the same way as the mercurous and mercuric salts. Some chemists regard the cuprous salts as containing monovalent copper. It is preferable, however, to represent them as compounds of the divalent double atom Cu_2.

‡ This ammoniacal solution of cuprous chloride also absorbs carbon monoxide, forming a compound believed to have the composition $COCu_2Cl_2,2H_2O$.

KI produces a yellowish-white precipitate of cuprous iodide, Cu_2I_2—

$$Cu_2Cl_2 + 2KI = Cu_2I_2 + 2KCl$$

Cupric iodide is unknown. When KI is added to a solution of a cupric salt, *cuprous* iodide is thrown down, and iodine is liberated, which colours the liquid brown—

$$2CuCl_2 + 4KI = Cu_2I_2 + 4KCl + I_2$$

In the presence of a reducing agent, such as a ferrous salt, or sulphurous acid, the cupric salt is first reduced to the *cuprous* state, which with the KI then gives cuprous iodide without separation of iodine—

$$2CuCl_2 + 2FeCl_2 = 2FeCl_3 + Cu_2Cl_2$$
$$2CuCl_2 + H_2SO_3 + H_2O = H_2SO_4 + 2HCl + Cu_2Cl_2$$

KCy gives a white precipitate of Cu_2Cy_2; soluble in excess of KCy, giving a double cyanide, $Cu_2Cy_2,6KCy$.

[*Cupric* cyanide, although known, is very unstable, hence when KCy is added to a cupric salt, the cupric cyanide, even if formed, quickly decomposes, and a mixture or compound of cuprous cyanide and cupric cyanide is produced. As with the iodide, if reducing agents are present, cuprous cyanide alone is produced.]

Separation of the Metals of Group II.—Division 1.

The separation of these metals is based upon—

1. The difference in the behaviour of their sulphides towards nitric acid; sulphides of Cu, Cd, and Bi being dissolved, while those of Hg and Pb are either not dissolved or are changed into other insoluble compounds.

2. The solubility of the hydroxides of Cd and Cu in NH_4HO, and the insolubility of $Bi(HO)_3$.

3. The solubility of *copper sulphide* in KCy, and the insolubility of CdS.

The solution containing salts of these metals is acidified by the addition of a few drops of dilute HCl,* and a stream of H_2S is

It likewise absorbs acetylene, C_2H_2, producing a red precipitate of cuprous acetylide; thus—

$$Cu_2Cl_2,2NH_3 + H_2O + C_2H_2 = Cu_2C_2,H_2O + 2NH_4Cl$$

* In the ordinary course of analysis, the metals of Group I. are thereby precipitated as chlorides; nearly the whole of the lead will therefore be removed before Group II. is examined. When the exercise is confined to this group, any precipitate of $PbCl_2$ obtained may be removed by filtration and examined separately.

allowed to bubble moderately slowly through the solution *until precipitation is complete* (see Precipitation, p. 7). During the process the liquid should be frequently stirred with the tube delivering the gas. After filtration, the solution should be diluted with water, and H_2S should be again passed through the liquid for a moment or two, to make sure that the precipitation has been complete.

The **precipitate** contains the sulphides of all the metals of the division. It should be well washed,* and then transferred to a small porcelain dish with the least possible quantity of water. About an equal volume of strong HNO_3 is then added, and the mixture boiled until no further dissolving action can be detected. The mixture is then diluted, and a few drops of dilute H_2SO_4 added. Before filtering, the mixture should be cooled.

The **residue** may contain HgS (*black*), $Hg(NO_3)_2$,2HgS (*white*), and $PbSO_4$ (*white*). Boil with a solution of ammonium acetate.

The **residue.** Dissolve in the least quantity of *aqua regia*. Boil to expel chlorine, and neutralise with NaHO.‡ Acidify with HCl, and introduce a strip of clean copper, which will become coated with a silvery deposit of mercury.

The **solution.** Add K_2CrO_4. A yellow precipitate of $PbCrO_4$.

The **filtrate** contains the nitrates of Bi, Cd, and Cu. Add excess of NH_4HO, and boil.

The **precipitate** is white Bi_2O_3,H_2O.†

Confirm by dissolving in a few drops of HCl, and adding the solution drop by drop into a test-tube nearly filled with water. White BiOCl is precipitated.

The **solution** contains ammoniacal Cd and Cu compounds. The presence of Cu is seen by the blue colour. If blue, add KCy until colourless, and pass H_2S. Yellow CdS precipitated.

If copper is absent, H_2S may be added at once.

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* Unless HCl (and soluble chlorides) be washed out of this precipitate, the addition of HNO_3 will result in the formation of a little *aqua regia*, and this will dissolve a portion of the mercuric sulphide.

† If any lead sulphate escaped precipitation in the previous step, or if any of the mercuric sulphide was dissolved (see previous note), compounds of these metals will be here thrown down by NH_4HO. Hence it is necessary to confirm Bi as indicated.

‡ This step is necessary, in order to remove HNO_3, the presence of which might prevent the deposition of Hg.

CHAPTER IX.

Reactions of the Metals of Group II.—Division 2.

Arsenic, Antimony, Tin [Gold, Platinum].

The two elements arsenic and antimony belong to the same natural family. Tin, on the other hand, is more nearly related to lead. The three elements are associated together in the same analytical group, for the reason that they possess in common the property of forming "thio" acids, whose alkaline salts are soluble in water; namely, thio-arsenites, thio-antimonites and thio-stannates. In other words, the sulphides of these metals are soluble in alkaline sulphides.

Arsenic, As.

Dry Reactions.—Compounds of arsenic are easily reduced and the element obtained in the "metallic" state, by heating them with suitable reducing agents.

Thus, when heated upon charcoal with Na_2CO_3 and KCy, arsenical compounds are reduced; but the metal, being extremely volatile and readily combustible, is for the most part burnt to arsenious oxide, As_4O_6, which passes off as a white fume. At the same time some of the vapour of the element itself is carried away with the fumes of the oxide, and is readily recognised by its strong, unpleasant, and characteristic garlic-like odour. Arsenic cannot be melted by heat after the manner of most metals, but passes from the solid to the vaporous states without liquefying; hence it never yields metallic globules upon the charcoal.

The reduction may be made by heating the arsenic compound in a glass tube with KCy, or a mixture of Na_2CO_3 and KCy. The reaction is conveniently studied by using arsenious oxide. A small fragment (about the size of a pin's head) is placed in a narrow test-tube * and covered by adding a mixture of Na_2CO_3 and KCy (equal

* For such experiments small test-tubes $4 \times \frac{5}{16}$ inches answer admirably. Bulb tubes are neither necessary nor desirable.

parts), the materials being as dry as possible. The total quantity of material in the tube should not occupy more space than is shown in Fig. 12. On the application of a gentle heat, the first effect will be the expulsion of moisture from the imperfectly dried materials,

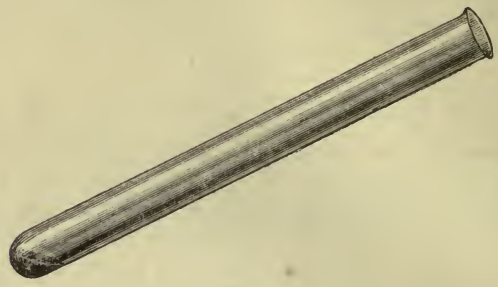

FIG. 12.

which condenses upon the sides of the tube. This may be driven up the tube by gently warming it, and finally removed by introducing a "spill" of blotting-paper. When no more moisture collects, the mixture may be steadily heated in the tip of a small Bunsen flame. The arsenic under these circumstances is vaporised without undergoing combustion, and sublimes upon the tube as a metallic mirror. Sufficient of the vapour escapes condensation to enable the strong garlic odour to be detected.

The reaction which takes place may be expressed by the equation—

$$As_4O_6 + 6KCy = As_4 + 6KOCy$$

The oxide of arsenic may be reduced by being heated with charcoal alone in a glass tube, when a metallic sublimate is also obtained. In this case it is necessary to cover the arsenic compound with a layer of charcoal, which should be strongly heated before the oxide of arsenic becomes hot, so that the vapour shall pass through the heated carbon; otherwise the arsenious oxide might be entirely volatilised before the carbon had become hot enough to reduce the compound.

WET REACTIONS.—The element arsenic has little or no claim to be ranked as a metal in the strict acceptation of the term. Being *like* a metal in appearance and in some of its physical properties, it is usually called a *metalloid*. In the natural family to which it belongs, it stands between phosphorus and nitrogen on the one

hand, and antimony and bismuth on the other, showing in its chemical habits a strong similarity to phosphorus.

It forms two oxides, both of which are *acidic* in their character; and all the salts of arsenic are such as contain this element in the acidic or negative portion of the molecule, united with other metals as the base; such, for example, as the arsenites and arsenates of various metals. No oxysalts of arsenic are known in which the element plays the part of a base, such as nitrate, sulphate, carbonate, etc., of arsenic.

(*a*) **Arsenious compounds,** derived from arsenious oxide, As_4O_6.* The arsenites of sodium, potassium, and ammonium alone are soluble in water. For the following reactions, potassium arsenite, K_3AsO_3, or a solution of As_4O_6 in dilute HCl, may be employed.

H_2S or $(NH_4)_2S$ precipitates from slightly acid solutions yellow arsenious sulphide, As_2S_3, soluble in excess of ammonium sulphide, giving ammonium thio-arsenite; thus—

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$

With yellow ammonium sulphide (polysulphide) the arsenious sulphide is dissolved, with the formation of ammonium *thio-arsenate*, the As_2S_3 first uniting with the sulphur of the polysulphide to form As_2S_5. From this solution the higher sulphide is precipitated on the addition of an acid. If H_2S be passed through an aqueous solution of As_4O_6 no precipitate is produced, but the liquid becomes yellow owing to the presence of arsenious sulphide in solution in the colloidal state. The addition of HCl causes the precipitation of the yellow sulphide. From neutral or alkaline solutions, H_2S (or $(NH_4)_2S$) gives no precipitate, as under these circumstances the soluble thio salt is produced. The addition of an acid decomposes the thio salt, and arsenious sulphide is thrown down. The reactions may be expressed thus—

$$K_3AsO_3 + 3H_2S = K_3AsS_3 + 3H_2O$$
$$2K_3AsS_3 + 6HCl = 6KCl + 3H_2S + As_2S_3\dagger$$

Arsenious sulphide is soluble in caustic alkalies and ammonia, also

* The acid corresponding to this oxide is not known. Three series of salts are known, which may be considered as being derived from the three hypothetical acids—ortho-arsenious acid, H_3AsO_3; pyro-arsenious acid, $H_4As_2O_5$; and metarsenious acid, $HAsO_2$.

† The hypothetical thio-arsenious acid, H_3AsS_3, may be supposed to be first formed, and to at once split up into the thio-anhydride As_2S_3 and into H_2S, just as on the addition of an acid to a carbonate the unstable carbonic acid H_2CO_3 breaks up into the anhydride CO_2 and water.

in ammonium carbonate, forming in each case a mixture of arsenite and thio-arsenite of the alkali ; thus—

$$As_2S_3 + 6KHO = K_3AsO_3 + K_3AsS_3 + 3H_2O$$
$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3CO_2$$

On the addition of acid, the mixed arsenite and thio-arsenite are decomposed, and arsenious sulphide is reprecipitated—

$$K_3AsO_3 + K_3AsS_3 + 6HCl = 6KCl + 3H_2O + As_2S_3$$

Arsenious sulphide is practically insoluble in HCl (contrast Sb_2S_3), but readily dissolves in HNO_3, or in HCl with addition of a crystal of $KClO_3$; being oxidised in each case into *arsenic* acid.*

$CuSO_4$ produces, in a solution of potassium arsenite, a green precipitate of hydrogen cupric arsenite, $HCuAsO_3$; † soluble in ammonia and caustic alkalies. If the solution be boiled, the *arsenite* is oxidised to *arsenate* at the expense of the copper, which is thereby reduced to cuprous oxide, and precipitated in this form ; thus—

$$2CuSO_4 + K_3AsO_3 + 4KHO = K_3AsO_4 + 2K_2SO_4 + 2H_2O + Cu_2O$$

$AgNO_3$ precipitates, from a solution of potassium arsenite, pale-yellow silver arsenite, Ag_3AsO_3, soluble both in NH_4HO and in HNO_3. If the precipitate be dissolved in either of these solvents, it can only be reprecipitated by neutralisation with the other, when the utmost care has been taken to avoid excess of the first, because the silver arsenite is soluble also in ammonium nitrate. When the ammoniacal solution is boiled for some time, metallic silver is precipitated, and the *arsenite* is oxidised to *arsenate.* The solution of silver arsenite in ammonia, and the decomposition on boiling, may be expressed by the following equations :—

$$Ag_3AsO_3 + 2NH_4HO = (NH_4)_2AgAsO_3 + Ag_2O \ddagger + H_2O$$
$$(NH_4)_2AgAsO_3 + Ag_2O = (NH_4)_2AgAsO_4 + Ag_2$$

Precipitation by Copper (Reinsch's test).—If a strip of clean copper foil be introduced into a solution of arsenious oxide in HCl, or an arsenite acidified with the same acid, and the mixture be

* The *modus operandi* of this oxidation of the sulphide by HCl and $KClO_3$ is that the chlorine first converts the sulphide into arsenic trichloride, which, in presence of water, forms arsenious acid, and that the chlorine oxidises this into arsenic acid. The changes may be thus expressed—

(1) $As_2S_3 + 3Cl_2 = 2AsCl_3 + 3S$
(2) $2AsCl_3 + 6H_2O = 6HCl + 2H_3AsO_3$
(3) $H_3AsO_3 + H_2O + Cl_2 = 2HCl + H_3AsO_4$

† Used as a pigment, under the name of *Scheele's green.*
‡ Ag_2O dissolves in ammonia.

warmed, metallic arsenic is deposited upon the copper, at the same time uniting with it, forming copper arsenide, Cu_5As_2. If the copper be then dried, and gently heated in a dry test-tube, the arsenic will be volatilised, and at the same time oxidised, giving, therefore, a white crystalline sublimate of As_4O_6 (*contrast antimony*).

(*b*) **Arsen*ic* compounds,** derived from arsenic pentoxide, As_2O_5.* Arsenates of sodium, potassium, and ammonium are soluble in water.

H_2S.—From neutral or alkaline solutions of an arsenate no precipitate is produced, the soluble thio-arsenate being formed. The addition of HCl to this solution throws down the pentasulphide in the form of a yellow precipitate—

$$K_3AsO_4 + 4H_2S = 4H_2O + K_3AsS_4$$
$$2K_3AsS_4 + 6HCl = 6KCl + As_2S_5 + 3H_2S$$

From acidified solutions of an arsenate, H_2S gives a precipitate after a short time, which is either As_2S_5 or a mixture of As_2S_3 and S, depending upon conditions.

If the solution is strongly acid, and the gas is passed rapidly, the precipitate which slowly comes down is the pentasulphide. On the other hand, if the solution is less strongly acid, and the H_2S is passed slowly, the arsenic acid is first reduced to arsenious acid, with deposition of sulphur, and the arsenious acid as it forms is converted into arsenious sulphide ; thus—

(1) $H_3AsO_4 + H_2S = H_2O + S + H_3AsO_3$
(2) $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$

This reducing action of H_2S is very slow, therefore *complete precipitation requires considerable time.* Warming the liquid hastens the action. The addition of a more powerful reducing agent, such as sulphurous acid, produces the effect at once.

As_2S_5 dissolves in alkaline sulphides, forming thio-arsenates, similar to the thio-arsenites.

$CuSO_4$ gives a pale bluish precipitate of hydrogen cupric arsenate, $HCuAsO_4$. Soluble, like the corresponding arsenite, in ammonia ; but the copper is not reduced on heating the solution, for the reason that arsenates are incapable of any further oxidation —in other words, they do not act as reducing agents (*contrast arsenites*).

* Three arsen*ic* acids derived from this oxide are known, namely, ortho-arsenic acid, H_3AsO_4 ; pyro-arsenic acid, $H_3As_2O_7$; and metarsenic acid, $HAsO_3$. The two latter, when dissolved in water, are converted into the ortho-acid ; it is, therefore, only possible to have an aqueous solution of the ortho-acid.

$AgNO_3$ produces a chocolate-coloured precipitate of silver arsenate, Ag_3AsO_4, which, like the arsenite, dissolves in NH_4HO, in HNO_3, and in NH_4NO_3. If a mixture of silver arsenate and arsenite be carefully dissolved in HNO_3, avoiding any excess, and then ammonia added drop by drop, the silver arsenate is precipitated first (recognised by its chocolate colour), and afterwards the yellow arsenite.

The ammoniacal solution of silver arsenate is not reduced on boiling, for the same reason that the copper salt is not reduced (*contrast arsenites*).

$MgSO_4$, in presence of NH_4Cl and NH_4HO, gives a white crystalline precipitate of ammonium magnesium arsenate, $(NH_4)MgAsO_4$*; practically insoluble in water. (The corresponding arsenite is known, but, being readily soluble in water, it is not produced by precipitation; hence this reaction serves to *distinguish an arsenate from an arsenite.*)

Marsh's Test.

In the presence of nascent hydrogen, both *arsenic* and *arsenious* compounds are reduced, and arsenuretted hydrogen is evolved. Thus, if a solution of arsenious or arsenic oxide be subjected to electrolysis, or if such solutions are introduced into a mixture from which hydrogen is being generated (*e.g.* zinc or magnesum with dilute acid), this compound of arsenic and hydrogen is produced. The action may be regarded as taking place in two stages, first the reduction of the arsenical compound to metallic arsenic, and then the further action of the nascent hydrogen upon this; thus—

$$As_4O_6 + 6H_2 = As_4 + 6H_2O$$
$$As_4 + 6H_2 = 4AsH_3$$

The properties of arsenuretted hydrogen which are made use of in analysis are the following:—

(1) The deposition of metallic arsenic† from the flame of the burning gas when a cold object is depressed upon the flame.

(2) The decomposition of the compound on passing through a heated tube, with deposition of an arsenical mirror.

* This compound closely resembles the corresponding phosphate, $(NH_4)MgPO_4$, and is precipitated under the same conditions. It may, however, be at once distinguished from the phosphate by dissolving it in HCl, and adding H_2S, when a yellow precipitate of As_2S_5 is produced.

† Recent experiments seem to prove that this deposit is in reality a solid hydride of arsenic AsH (Retgers, *Zeits. f. anorg. Chem.*, iv. 739).

(3) The action of the gas upon a solution of silver nitrate, resulting in the precipitation of metallic silver.

The reaction is made in a small hydrogen generating apparatus, preferably a Woulff's bottle, of about 200 cub. cms. capacity. In this hydrogen is slowly generated from zinc and dilute sulphuric acid, both materials being free from arsenic. To the exit-tube is attached a tube, drawn out of a piece of combustion tube in such a manner as to present one or two constricted places in its length, as shown in Fig. 13. As soon as the air is all expelled from the apparatus, the issuing hydrogen is inflamed.*

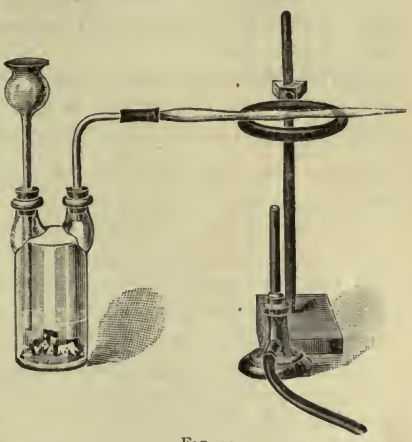

Fig. 13.

A small quantity of the arsenical solution is now introduced through the thistle-tube. The first effect of this is to cause the precipitation of arsenic upon the zinc ; which, constituting a voltaic couple, at once gives rise to a greatly increased rate of evolution of hydrogen.† The colour of the hydrogen flame will be seen to change, and to assume a lilac tint (resembling the colour given to a flame by potassium compounds), and at the same time white fumes of As_4O_6 escape from the tip of the flame. If now a porcelain dish be depressed upon the flame, a rich brown-black metallic-looking stain will be deposited. The deposit being volatile, and the flame very hot, the stain will again disappear if the flame be allowed to impinge for more than a moment or two on the same spot.

If the drawn-out tube be heated near one of the constrictions, the arsenuretted hydrogen will be decomposed as it passes the hot spot, and an arsenic mirror will be deposited in the tube.

* A small test-tube should be filled by upward displacement, and tested by a flame before igniting the gas at the exit-tube of the apparatus. As an additional precaution, it is well to throw a duster lightly over the Woulff's bottle before applying a light, so that, should an explosion happen, the broken glass will be prevented from flying about.

† On this account, it is necessary that the generation of hydrogen *before* adding the arsenic solution should be quite slow ; and also that the quantity of the arsenic solution added at a time should be small.

It will be noticed that the deposition takes place entirely on that part of the tube which is on the side of the flame farthest from the generating vessel * (antimony is deposited from its hydride on *both sides* of the heated spot).

Since antimony also forms a gaseous compound with hydrogen which gives similar stains,† it is necessary to employ further confirmatory tests.

1. The arsenic stains are readily dissolved by a solution of a hypochlorite. If, therefore, a solution of bleaching powder be poured over such stains they immediately disappear—

$$5Ca(OCl)_2 + 6H_2O + As_4 = 5CaCl_2 + 4H_3AsO_4$$

Or—

$$3Ca(OCl)_2 + 2H_2O + 2AsH = 3CaCl_2 + 2H_3AsO_4$$

Antimony stains do not dissolve in hypochlorite solutions.

2. When a stream of H_2S is passed through the tube containing the deposit of either arsenic or antimony, slightly warmed, in each case the sulphide is formed. Yellow arsenious sulphide volatilises along from the warm region and condenses on the cold distant part of the tube ; antimonious sulphide, reddish or nearly black, remains unmoved, being non-volatile. (If present together, they can in this way be separated.)

If a stream of gaseous HCl be now passed through the tube, antimonious sulphide is converted into antimonious chloride, which passes on with the HCl, and may be led into water and again precipitated as the red sulphide with H_2S. The yellow arsenious sulphide remains in the tube, being unattacked by HCl.

3. Arsenuretted hydrogen can also be distinguished from the antimony compound, by the difference in the behaviour of the two gases towards silver nitrate. When passed into the silver solution, each gas produces a black precipitate. In the case of arsenic this consists of metallic silver, while with antimony it consists of antimonide of silver ; thus—

$$6AgNO_3 + 3H_3O + AsH_3 = 3Ag_2 + 6HNO_3 + H_3AsO_3$$
$$3AgNO_3 + SbH_3 = SbAg_3 + 3HNO_3$$

If both antimony and arsenic were originally present, these two

* When the quantity of arsenic present is very minute, it will not be visible in the flame, neither may it be possible to obtain a stain on cold porcelain. But the formation of the mirror in the heated tube is a method by which extremely small traces of arsenic can be detected.

† The stains given by antimoniuretted hydrogen have a rather more velvety or sooty appearance, when deposited on porcelain from the flame, than those of arsenic.

precipitates will be produced together. On filtering, the arsenic (now as arsenious acid) goes into the filtrate along with the excess of silver nitrate used. Its presence may be detected by the cautious addition of ammonia, which causes the precipitation of yellow silver arsenite.

The antimony (as silver antimonide) remains on the filter; after being washed, it is boiled with a solution of tartaric acid.* The liquid thus obtained after filtration is acidulated with HCl, and antimonious sulphide precipitated by H_2S.

Fleitmann's Test.

When an arsenite, or a solution of arsenious oxide, is warmed in a test-tube with a solution of sodium hydroxide and metallic zinc, arseniuretted hydrogen is evolved, which can be detected by means of a piece of filter-paper moistened with silver nitrate held to the mouth of the tube. A black stain of precipitated silver is produced. Antimoniuretted hydrogen is not produced from antimony compounds under similar conditions.

Antimony, Sb.

DRY REACTIONS.—Antimony compounds may be reduced to metallic antimony by heating them with Na_2CO_3 and KCy upon charcoal. Globules of the metal are thus obtained, which burn in the blowpipe flame, producing white fumes of antimonious oxide, Sb_4O_6, the combustion being continued for a short time after removal from the flame. The charcoal at the same time receives a white incrustation. The bead of metal will be found to be very brittle, and, when broken, to exhibit a highly crystalline appearance. Antimony is unacted upon by dilute HCl or H_2SO_4. Nitric acid oxidises it into antimonic acid, or antimonious oxide, depending upon conditions of concentration.

WET REACTIONS.—Both in its physical properties and chemical relations antimony approaches more nearly to the true metals than is the case with arsenic. It forms two series of compounds, "antimonious" and "antimonic," which may be regarded as being derived respectively from the two oxides, antimonious oxide, Sb_4O_6, and antimony pentoxide, Sb_2O_5.

* Although ordinary metallic antimony is not soluble in tartaric acid, and is only slowly attacked by strong hydrochloric acid even when the metal is in the form of powder, nevertheless, when combined with silver as it is in the precipitate of silver antimonide, the antimony is comparatively easily dissolved by HCl, and dissolves when boiled in a strong solution of tartaric acid. In the latter case antimony tartrate, $(SbO)_2C_4H_4O_6$, goes into solution, leaving metallic silver. With HCl antimonious chloride is formed, and silver chloride remains.

It will be noticed that the deposition takes place entirely on that part of the tube which is on the side of the flame farthest from the generating vessel * (antimony is deposited from its hydride on *both sides* of the heated spot).

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(*a*) **Antimonious Compounds.**—In antimonious oxide we see the gradual fading away, so to speak, of the *acidic* properties exhibited by the corresponding oxides of arsenic and phosphorus (elements with which antimony is associated in the natural classification), and the beginnings of *basic* qualities. Thus, no acids corresponding to this oxide are known, and only a few salts (derived from the hypothetical metantimonious acid) have been obtained. Of these the best known is sodium metantimonite, obtained by dissolving the oxide in sodium hydroxide ; thus—

$$Sb_4O_6 + 4NaHO = 4NaSbO_2 + 2H_2O$$

On the other hand, this oxide unites with certain acids forming salts, in which the antimony—in combination with oxygen as the monovalent radical *antimonyl* (SbO)—takes the place of the positive or basilous element. Of these salts the tartrate, $(SbO)_2(C_4H_4O_6)$, and the double potassium tartrate (*tartar emetic*), $(SbO)K(C_4H_4O_6)$, are the most familiar—

$$Sb_4O_6 + 4HK(C_4H_4O_6) = 4(SbO)K(C_4H_4O_6) + 2H_2O$$

For the following reactions * an acid (HCl) solution of antimonious chloride may be employed.

KHO, NaHO, NH_4HO, as well as alkaline carbonates, precipitate antimonious oxide, Sb_4O_6 ; thus—

$$4SbCl_3 + 12KHO = Sb_4O_6 + 12KCl + 6H_2O$$
$$4SbCl_3 + 6K_2CO_3 = Sb_4O_6 + 12KCl + 6CO_2$$

The precipitate redissolves in excess of either potassium or sodium hydroxide, forming the respective metantimonites (equation above).

H_2O, added in considerable quantity to the acid solution of $SbCl_3$, gives a white precipitate of an oxychloride, SbOCl—

$$SbCl_3 + H_2O = 2HCl + SbOCl$$

This compound is at once distinguished from the similarly produced BiOCl, by the fact that the antimony oxychloride readily dissolves in tartaric acid, giving antimonyl tartrate ; thus—

$$2SbOCl + H_2(C_4H_4O_6) = (SbO)_2(C_4H_4O_6) + 2HCl$$

On boiling the precipitated oxychloride for some time with water, the whole of its chlorine is given up, and antimonious oxide is formed—

$$4SbOCl + 2H_2O = Sb_4O_6 + 4HCl$$

* Except that with $AgNO_3$, in which obviously the presence of chlorine would interfere.

H_2S and $(NH_4)_2S$ give a red or orange-red precipitate of antimonious sulphide, Sb_2S_3. Soluble in excess of ammonium sulphide. If yellow ammonium sulphide be employed, the thio salt of Sb_2S_5 is formed, and on acidifying the liquid, Sb_2S_5 is precipitated from it. Antimonious sulphide is soluble also in caustic alkalies, from which solution the trisulphide is again thrown on acidifying—

$$2Sb_2S_3 + 4KHO = 3KSbS_2 + KSbO_2 + 2H_2O$$
$$3KSbS_2 + KSbO_2 + 4HCl = 2Sb_2S_3 + 4KCl + 2H_2O$$

Antimonious sulphide is not dissolved by ammonia or by ammonium carbonate (*contrast arsenic*).

Antimonious sulphide is decomposed by hot hydrochloric acid—

$$Sb_2S_3 + 6HCl = SbCl_3 + 3H_2S$$

This reaction is the reverse of that by which the sulphide is formed. In this case, however, one of the products, namely the H_2S, is driven from the sphere of action as fast as it is generated.

$AgNO_3$, added to an alkaline solution of antimonious oxide, gives a black precipitate, consisting of silver oxide and metallic silver. The action takes place in two stages. The silver nitrate interacts with the caustic alkali present, giving silver oxide, and this in its turn gives up oxygen to the antimon*ite*, converting it into antimon*ate* ; thus—

$$2AgNO_3 + 2KHO = Ag_2O + 2KNO_3 + H_2O$$
$$KSbO_2 + Ag_2O = Ag_2 + KSbO_3$$

(*b*) **Antimonic Compounds.** — These are derived from the pentoxide, Sb_2O_5. This oxide is, however, so *feebly* acidic that it is not converted into antimonic acid by the action of water. Only two classes of antimonates are known (compare arsenates and phosphates), namely, pyro-antimonates (*e.g.* $K_4Sb_2O_7$) and met-antimonates (*e.g.* $KSbO_3$).

Potassium pyro-antimonate is readily soluble in water, while the sodium salt is difficultly soluble, hence the potassium compound is used as a reagent for sodium (p. 22).

KHO, NaHO, NH_4HO, as well as alkaline carbonates, give with an acid solution of antimony pentachloride a white precipitate consisting of metantimonic acid—

$$SbCl_5 + 5KHO = HSbO_3 + 5KCl + 2H_2O$$

H_2O, added in considerable quantity, produces the same precipitate *—

$$SbCl_5 + 3H_2O = HSbO_3 + 5HCl$$

From aqueous solutions of antimonates, the same precipitate is produced by acids—

$$KSbO_3 + HNO_3 = KNO_3 + HSbO_3$$

In the case of pyro-antimonates, the "pyro" acid is first produced, which then passes into the "meta" compound (footnote).

H_2S and $(NH_4)_2S$ produce with acidified solutions of antimonic compounds an orange-red precipitate consisting of Sb_2S_5, Sb_2S_3, and S in varying proportions.

The reducing action of the H_2S converts a portion of the antimonic compound to the antimonious state, from which by further action the antimonious sulphide is thrown down. The three following reactions, therefore, proceed simultaneously—

$$2KSbO_3 + 5H_2S = Sb_2S_5 + 5H_2O + K_2O$$
$$KSbO_3 + H_2S = S + KSbO_2 + H_2O$$
$$2KSbO_2 + 3H_2S = Sb_2S_3 + 3H_2O + K_2O$$

The action being carried on in *acid* solution, the K_2O is at once neutralised.

The precipitate behaves towards alkaline sulphides and caustic alkalies in a manner similar to that of Sb_2S_3; thus, with KHO potassium thio-antimonate (ortho) and antimonate (meta) are produced, from which an acid reprecipitates the Sb_2S_5—

$$4Sb_2S_5 + 18KHO = 5K_3SbS_4 + 3KSbO_3 + 9H_2O$$
$$5K_3SbS_4 + 3KSbO_3 + 18HCl = 4Sb_2S_5 + 18KCl + 9H_2O$$

$AgNO_3$ gives a white precipitate with aqueous solutions of antimonates, consisting of silver antimonate. The precipitate dissolves in ammonia (*distinction between "antimonic" and "antimonious" compounds*).

KI.—When antimonic compounds, in presence of HCl, are boiled with a solution of KI, the antimonic compound is reduced to the "antimonious" state, and iodine is liberated. The free iodine, if in quantity, colours the solution brown; if in small quantity, it may be recognised by the formation of the blue colour

* This action takes place in two stages, pyro-antimonic acid being first formed, which loses a molecule of water and passes into the more stable metantimonic acid; thus—

$$2SbCl_5 + 7H_2O = 10HCl + Sb_2O_5,2H_2O \; (= H_4Sb_2O_7)$$
$$Sb_2O_5,2H_2O - H_2O = Sb_2O_5,H_2O = 2HSbO_3$$

with starch (*distinction between "antimonic" and "antimonious" compounds*)—

$$KSbO_3 + 2HCl + 2KI = KSbO_2 + 2KCl + H_2O + I_2$$

Or, in the case of the oxide or hydrated oxide—

$$Sb_2O_5,H_2O + 4HCl + 4KI = Sb_2O_3,H_2O + 4KCl + 2H_2O + 2I_2$$

Precipitation of Metallic Antimony.—Antimony compounds (of either state of oxidation), when in acid (HCl) solution, readily deposit metallic antimony by galvanic action. The test is applied in the following way : one or two drops of the acid solution are placed upon a piece of clean platinum foil, and a small fragment of zinc immersed in the liquid. Immediately a black stain is produced upon the platinum by the deposition of metallic antimony. Even very dilute solutions give the stain, hence the test is a delicate one. HCl has no action upon the deposit, but warm HNO_3 instantly attacks it, giving antimonic acid (hence the absence of nitric acid from the solution before applying the test is desirable).

Antimoniuretted hydrogen is evolved when antimony compounds are acted upon by nascent hydrogen. The compound undergoes reactions similar to those of the corresponding arsenic compound. The methods for distinguishing between them are described under arsenic.

Tin, Sn.

Dry Reactions.—Compounds of tin are reduced to the metallic state by being heated on charcoal with Na_2CO_3 and KCy in the reducing flame. A portion of the metal is oxidised by the flame, and produces a white incrustation of SnO_2 upon the charcoal; this, on being moistened with cobalt nitrate and reheated, assumes a greenish appearance.

The beads of reduced metal are malleable (therefore easily distinguished from Bi or Sb), but are not soft enough to mark paper in the manner of lead.

Tin dissolves in hot strong HCl, forming stannous chloride, $SnCl_2$, hydrogen being evolved. Hot H_2SO_4 converts it into stannous sulphate, $SnSO_4$, and gives off SO_2.

Cold dilute HNO_3 dissolves tin, forming stannous nitrate, $Sn(NO_3)_2$, and ammonia; ordinary strong acid (sp. gr. 1·24) attacks it violently, converting it into white metastannic acid, $H_{10}Sn_5O_{15}$.

Wet Reactions.—Tin forms two classes of compounds, distinguished as "stannous" and "stannic," derived respectively from stannous oxide, SnO, and stannic oxide, SnO_2.

(*a*) **Stannous Compounds.**—Stannous oxide is basic in its character, giving with acids the stannous salts, in which the metal is divalent. Of these the chloride, sulphate, and nitrate are soluble in water. The chloride is most common.

KHO, NaHO, NH_4HO, as well as alkaline carbonates, give with stannous chloride a white precipitate of hydrated stannous oxide (basic hydroxide) ; thus—

$$2SnCl_2 + 4KHO = 2SnO,H_2O + 4KCl + H_2O$$

The precipitate is soluble in excess of KHO or NaHO (but not in the other precipitants), forming alkaline *stannites;* thus—

$$2SnO,H_2O + 4KHO = 2K_2SnO_2 + 3H_2O$$

H_2S or $(NH_4)_2S$ gives, with dilute solutions of stannous chloride, a deep brown precipitate of stannous sulphide. Soluble in yellow ammonium sulphide, with the formation, not of a *thio-stannite*, but *thio-stannate.* (Colourless ammonium sulphide is almost without action upon it.) Stannic sulphide, SnS_2, is thrown down upon the addition of acids.

Stannous sulphide dissolves in caustic alkalies, forming a stannite and thio-stannite—

$$2SnS + 4KHO = K_2SnO_2 + K_2SnS_2 + 2H_2O$$

From this, on addition of acid, stannous sulphide is again precipitated—

$$K_2SnO_2 + K_2SnS_2 + 4HCl = 4KCl + 2H_2O + 2SnS$$

Stannous sulphide is insoluble in ammonium carbonate. Boiling HCl converts it into $SnCl_2$; while *aqua regia* oxidises it to stannic chloride, $SnCl_4$.

Oxidation of Stannous Compounds.—These substances readily pass, by oxidation, into stannic compounds ; they therefore act the part of powerful *reducing* agents in a number of reactions, of which the following are important :—

(1) **Mercuric chloride,** in the presence of small quantities of stannous chloride, is reduced to mercurous chloride, which is thrown down as a white precipitate. With excess of the stannous salt, and on warming, the precipitate is further reduced, and becomes grey through the separation of metallic mercury—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

(2) **Ferric salts** are reduced to the "ferrous" state ; thus,

ferric sulphate, in the presence of hydrochloric acid, gives ferrous sulphate and stannic chloride—

$$Fe_2(SO_4)_3 + SnCl_2 + 2HCl = 2FeSO_4 + H_2SO_4 + SnCl_4$$

(3) **Gold chloride,** in the presence of acid, is reduced to metallic gold—

$$2AuCl_3 + 3SnCl_2 = 3SnCl_4 + 2Au$$

In *neutral* solutions, a reddish or purple precipitate (or coloration, if very dilute) is produced, known as *purple of Cassius.* Its formation is promoted by the presence of a little stannic chloride in the stannous compound. Its composition is believed to be expressed by the formula $Au_2,3SnO_2$. Acids convert it into metallic gold and a stannic salt.

(4) **Cupric salts, chromates,** and **permanganates** are reduced respectively to cuprous, chromic, and manganous salts; thus—

$$2KMnO_4 + 16HCl + 5SnCl_2 = 2KCl + 2MnCl_2 + 8H_2O + 5SnCl_4$$

(5) **Bismuth salts** are reduced in alkaline solutions, with the precipitation of black bismuthous oxide, Bi_2O_2 or BiO, and the oxidation of the stannite to stannate. Thus, if bismuth chloride or nitrate (salts derived from Bi_2O_3) are added to an alkaline solution of stannous oxide (*i.e.* to a solution of potassium stannite), the following reaction takes place :—

$$K_2SnO_2 + 6KHO + 2Bi(NO_3)_3 = K_2SnO_3 + 6KNO_3 + 3H_2O + 2BiO$$

The reaction will be simpler if we have regard only to the oxide of bismuth, from which the nitrate is derived—

$$K_2SnO_2 + Bi_2O_3 = 2BiO + K_2SnO_3$$

(6) An aqueous solution of stannous chloride gradually absorbs atmospheric oxygen, being converted partly into stannic chloride, and a white insoluble basic chloride; thus—

$$3SnCl_2 + H_2O + O = SnCl_4 + SnCl_2,SnO,H_2O$$

(*b*) **Stannic Compounds.**—Stannic oxide, SnO_2, may be regarded as being both a "basic" and an acidic oxide, for, although itself insoluble in either acids or alkalies, we may consider both the *stannic salts* and the *stannates* as being derived from this oxide. The most important stannic salt is the chloride, $SnCl_4$. A solution of this compound in hydrochloric acid may be used for the following reactions :—

KHO, NaHO, NH_4HO, as well as alkaline carbonates, give a white precipitate of hydrated stannic oxide, or stannic acid, SnO_2,H_2O, or H_2SnO_3* ; thus—

$$SnCl_4 + 4NaHO = H_2SnO_3 + 4NaCl + H_2O$$

Soluble in HNO_3 and in HCl. Soluble in KHO and NaHO, with formation of the respective stannates, K_2SnO_3, and Na_2SnO_3 ; thus—

$$H_2SnO_3 + 2NaHO = Na_2SnO_3 + 2H_2O$$

H_2S or $(NH_4)_2S$ precipitates yellow stannic sulphide, SnS_2 (with H_2S the precipitate appears nearly white at first, and is only complete in dilute solutions). The precipitate is soluble in caustic alkalies, in ammonium sulphide, and sulphides of the alkalies, forming thio-stannates ; thus—

$$3SnS_2 + 6KHO = 2K_2SnS_3 + K_2SnO_3 + 3H_2O$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

From these solutions the yellow stannic sulphide is reprecipitated on the addition of HCl—

$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + SnS_2 + H_2S$$

Stannic sulphide is insoluble in ammonium carbonate, but dissolves in hot strong HCl. Stannic oxysalts, such as the nitrate or sulphate, are unstable in aqueous solution, and are decomposed into stannic or metastannic acid. Therefore, when by double decomposition such oxysalts might be expected to form, the result is the precipitation of one or both of these stannic acids. Thus, when sulphuric acid is added to stannic chloride and the solution diluted with water, the action may be represented by the two equations—

(1) $SnCl_4 + 2H_2SO_4 = 4HCl + Sn(SO_4)_2$

(2) $[Sn(SO_4)_2 + 3H_2O = 2H_2SO_4 + H_2SnO_3] \times 5$ to represent metastannic acid.

A similar precipitation takes place when neutral salts of the alkalies are employed, such as sodium sulphate or ammonium nitrate ; thus—

* Meta-stannic acid, the white compound obtained by the action of nitric acid upon tin, is expressed by the same formula multiplied by five, $5(H_2SnO_3)$, or $H_{10}Sn_5O_{15}$. It forms salts by the replacement of *two* hydrogen atoms only, as is the case with stannic acid ; their composition may therefore be expressed by the formula (taking potassium metastannate as an example), $K_2SnO_3,4SnO_2,4H_2O$. Boiling (or fusing) with caustic alkalies converts meta-stannates into stannates ; thus—

$$K_2SnO_3,4SnO_2,4H_2O + 8KHO = 5K_2SnO_3 + 8H_2O$$

(1) $SnCl_4 + 4(NH_4)NO_3 = 4NH_4Cl + Sn(NO_3)_4$
(2) $[Sn(NO_3)_4 + 3H_2O = 4HNO_3 + H_2SnO_3] \times 5$

Precipitation of Metallic Tin.—When zinc is immersed in an acid solution of stannous or stannic chloride, the tin is displaced by the zinc, and precipitated as a grey-black deposit upon the surface of the zinc; or, if the whole of the zinc becomes dissolved, the tin is left as a scaly powder. It may be collected, and, after being washed, dissolved in hot hydrochloric acid. Tin produces no stain upon platinum, as is the case with antimony; and, again, differs from this metal in dissolving in HCl.

Gold and Platinum.

Although these two metals do not belong to the class of *rare* elements, nevertheless it is very rarely that the student is called upon to analyse mixtures containing either of them. In actual practice these metals are met with only in the analysis of alloys, where their presence is probably more than suspected at the outset. Neither gold nor platinum are soluble in either sulphuric, nitric, or hydrochloric acid; but they readily dissolve in a mixture of nitric and hydrochloric acids, yielding the chlorides $AuCl_3$ and $PtCl_4$ respectively. Comparatively few simple salts containing gold or platinum are known, and their compounds generally are characterised by the extreme readiness with which they are reduced to the metallic state.

H_2S or $(NH_4)_2S$ gives, with solutions of $AuCl_3$ and $PtCl_4$, precipitates of the sulphides. In the case of platinum the precipitation is slow. Auro-auric sulphide, Au_2S,Au_2S_3, or AuS (black), and platinic sulphide, PtS_2 (also black)—

$$8AuCl_3 + 9H_2S + 4H_2O = 24HCl + H_2SO_4 + 2(Au_2S,Au_2S_3), \text{ or } 8AuS$$
$$PtCl_4 + 2H_2S = 4HCl + PtS_2$$

If the gold solution be boiling, the reduction goes further, and metallic gold is thrown down—

$$8AuCl_3 + 3H_2S + 12H_2O = 24HCl + 3H_2SO_4 + 8Au$$

The sulphides of both metals are insoluble in HCl and HNO_3, but dissolve in *aqua regia*.

AuS dissolves in ammonium sulphide and in sulphides of the alkalies, forming thio-aurates. PtS_2, unmixed with other sulphides, does not dissolve in ammonium sulphide; but in the presence of other sulphides of the group, it is partially dissolved.* From the

* Owing to the fact that PtS_2 is only *partially* dissolved by ammonium sulphide, if platinum happened to be present in a mixture which was undergoing systematic analysis, a portion of the sulphide would pass into Group II. Division 2, along with As, Sb, Sn, Au; and a part of it would remain in Division 1, along with Hg, Bi, Cu, Cd, being ultimately found with the HgS, insoluble in HNO_3. For this reason it is more advantageous to remove platinum (and also gold) before the separation of Group II. is commenced, as explained on p. 107.

solution in both cases, the sulphides are reprecipitated on the addition of HCl.

KHO.—Neither the hydroxides nor carbonates of the alkalies give any precipitate with moderately dilute solutions of $AuCl_3$ or $PtCl_4$.

From a *concentrated* solution of $AuCl_3$, NH_4HO gives an orange-red precipitate of *fulminating gold*, $(NH_3)_2,Au_2O_3$; while KHO produces a brown precipitate of hydrated auric oxide, $Au_2O_3,3H_2O$, or $Au(HO)_3$. This precipitate is soluble in excess of potash, yielding potassium aurate, K_2O,Au_2O_3, or $KAuO_2$.

Both $AuCl_3$ and $PtCl_4$ form double salts with alkaline chlorides (chloro-aurates and chloro-platinates). Ammonium chloro-aurate, $NH_4Cl,AuCl_3$, or NH_4AuCl_4, is soluble in water; while ammonium chloro-platinate, $2NH_4Cl,PtCl_4$, or $(NH_4)_2PtCl_6$, is moderately insoluble, and is produced by precipitation when ammonium chloride is added to a moderately strong solution of $PtCl_4$.

Gold and platinum are readily reduced from their compounds (more especially gold) and precipitated in the metallic state, and their most characteristic reactions are based upon this fact. Thus—

1. *Ferrous sulphate* gives a brown precipitate of metallic gold; in weak solutions a bluish coloration—

$$AuCl_3 + 3FeSO_4 = Fe_2(SO_4)_3 + FeCl_3 + Au$$

With platinum the action only takes place on prolonged boiling—

$$3PtCl_4 + 12FeSO_4 = 4Fe_2(SO_4)_3 + 4FeCl_3 + 3Pt$$

2. *Oxalic acid*, on being gently warmed with $AuCl_3$, causes the deposition of the metal either as a scaly precipitate or as a coherent gold film upon the glass, according to the conditions of the experiment. Platinum is not reduced by oxalic acid—

$$2AuCl_3 + 3C_2H_2O_4 = 6CO_2 + 6HCl + 2Au$$

3. *Potassium nitrite* reduces $AuCl_3$, being itself converted into nitrate—

$$2AuCl_3 + 3H_2O + 3KNO_2 = 3KNO_3 + 6HCl + 2Au$$

With platinum no precipitate forms at first, but on standing, yellow crystals are deposited of a double nitrite of potassium and platinum (one of the few oxysalts of platinum known) containing platinum in the *platinous* condition, $2KNO_2,Pt(NO_2)_2$, or $K_2Pt(NO_2)_4$*—

$$PtCl_4 + 5KNO_2 + H_2O = K_2Pt(NO_2)_4 + 2KCl + 2HCl + KNO_3$$

4. *Stannous chloride* gives with $AuCl_3$ a precipitate or coloration (depending upon concentration) varying in colour from reddish-brown to purple. The compound is known as *purple of*

* The platino-nitrites are remarkable in that the platinum they contain does not answer to the ordinary tests for that metal, just as the iron in ferrocyanides is not detected by the ordinary reactions for iron.

Cassius, and its composition is not known with certainty. The presence of a small quantity of stannic chloride (such as is always present in a solution of stannous chloride except when quite freshly made) facilitates the production of the purple.

With $PtCl_4$ a brown colour is produced, by the reduction of the platinum chloride to platinous chloride, $PtCl_2$.

In analysis, when gold and platinum are present, it is preferable to remove them before the precipitation of Group II. by sulphuretted hydrogen. The gold is precipitated in the metallic state by oxalic acid, and the solution is evaporated down with ammonium chloride, which causes the precipitation of the platinum as ammonium platinum chloride, $2NH_4Cl,PtCl_4$.

Separation of the Metals of Group II.—Division 2.

The separation of Group II. from Groups III., IV., and V. depends upon the precipitation of their sulphides from acid solutions.

The separation of Division 1 from Division 2 is based upon the solubility of the sulphides of the latter in ammonium sulphide or in caustic alkalies.

The separation of the metals As, Sb, and Sn from each other is based upon—

(1) The insolubility of arsenic sulphide in hydrochloric acid (or its solubility in ammonium carbonate), whereby arsenic is separated from Sb and Sn.

(2) The solubility of metallic tin, and insolubility of antimony, in hydrochloric acid.

The solution, if neutral or alkaline, is acidified with HCl,* and sulphuretted hydrogen passed through (as described on p. 88) until the precipitation of the metals of Group II. is complete. The precipitate is thoroughly washed (in order to make the separation from Groups III., IV., and V. complete), and is then transferred to a small beaker, and gently warmed with yellow ammonium sulphide for a few minutes.† The liquid is then filtered. The residue consists of the undissolved sulphides of the metals of Group II., Division 1.

* If the solution under examination is alkaline, it may contain thio salts of As, Sb, or Sn; the addition of HCl will result in the precipitation of the sulphides of these metals. If it is neutral, basic salts of antimony might be precipitated at first, but redissolve on warming with a slight excess of the acid.

† Ammonium sulphide dissolves CuS to a slight extent (see Reactions, p. 85), hence, if this element is present, a small quantity of it will find its way into the solution along with As, Sb, and Sn.

The solution contains the thio salts of As, Sb, and Sn. It should be somewhat diluted, and hydrochloric acid added drop by drop until the sulphides are completely reprecipitated; then filtered and washed. The precipitate is then transferred to a boiling-tube with a small quantity of HCl, and boiled for a few moments until H_2S is no longer given off. It is then diluted and filtered.

The **residue** consists of arsenic sulphide and sulphur.

Confirm by dissolving in HCl with a crystal of $KClO_3$, and applying special reactions for arsenic, such as Fleitman's or Reinsch's test.*

The **solution.** Pour a few drops upon a piece of platinum foil, and add a fragment of zinc. A black stain indicates Sb. If antimony is present, place a strip of zinc along with the platinum foil in the remainder of the solution, until all the antimony and tin are thrown down. Collect the deposit and boil it with strong HCl, and filter. Test the filtrate for Sn by means of $HgCl_2$.

APPENDIX TO CHAPTER IX.

THE RARE METALS OF GROUP II.

Four of these metals belong to Division 1 of this group, their sulphides being insoluble in ammonium sulphide; these are—

Ruthenium, Rhodium, Palladium, and Osmium.

The remaining members form sulphides which are soluble in ammonium sulphide, and they therefore belong to the antimony, arsenic, and tin subdivision, namely—

Iridium, Tellurium, Selenium, Molybdenum.

The composition of the precipitates which are thrown down by the group-reagent, is the following :—

Ru_2S_3, Rh_2S_3, PdS, OsS } Insoluble in ammonium sulphide.

Ir_2S_3, TeS_2, Se, MoS_3 } Soluble in ammonium sulphide.

* In order to ascertain the condition of oxidation in which the arsenic originally existed in the substance under analysis, special tests must be applied to the solution before it has been exposed either to reducing or oxidising influences, as in the case of iron.

The metals of the first division, together with iridium in the second section, belong to the natural family of elements known as the *platinum metals*, because they all occur associated together in *platinum ore*. Of these, *ruthenium* and *rhodium* are the most rare.*

Palladium.—This metal, in the elemental state, is readily distinguished from all the others of the platinum group by its ready solubility in warm nitric acid. The other *platinum metals* are unacted upon by any ordinary acid. *Aqua regia* is without action upon *rhodium* and *iridium;* it acts with slowness upon *ruthenium*, and readily dissolves *platinum*, forming the chloride, while it converts *osmium* into the tetroxide.

When palladium is dissolved in nitric acid, the compound formed is palladious nitrate, $Pd(NO_3)_2$. If the solution be diluted with water, especially if the amount of free acid present is only small, a brown-coloured precipitate is produced, consisting of a basic nitrate. Palladious sulphide, PdS, produced by the group reagent, is black.

Mercuric cyanide, $HgCy_2$, gives a yellowish precipitate of palladious cyanide, $PdCy_2$; slightly soluble in hydrochloric acid, readily soluble in ammonia and in potassium cyanide. The precipitate is distinguished from other metallic cyanides by the reaction common to all palladium salts, namely, that when heated they decompose, leaving spongy metallic palladium.

Potassium iodide, KI, gives a characteristic black precipitate of palladious iodide, PdI_2. Palladious salts are readily reduced to the metallic state either by heat or by the action of reducing agents.

Osmium.—The compound of this rare element which is most commonly met with is the so-called *osmic acid*, which is employed in the preparation of microscopic sections of animal tissues. This compound is the tetroxide, OsO_4, or osmic anhydride.

It is characterised by its extremely low melting-point (about 40°) and boiling-point (100°), and by the peculiar and irritating vapour which it gives. The vapour exerts a most injurious effect upon the eyes, and is extremely poisonous.

This vapour is given off when any osmium compound is heated with nitric acid, and serves as a characteristic test for the element.

The tetroxide is soluble in water, giving a neutral solution which has powerful oxidising properties; it bleaches indigo, liberates iodine from potassium iodide, and oxidises ferrous sulphate and alcohol, the osmium compound being reduced to the state of hydrated dioxide, $OsO_2{,}2H_2O$ (or $Os(HO)_4$), which is thrown down as a black precipitate.

Sulphurous acid, or a sulphite added to the solution, produces a series of colour-changes from yellow to green and lastly blue, the colour of the osmious sulphite, $OsSO_3$, which then separates out.

Iridium.—This metal differs from platinum in not being dissolved by *aqua regia*. When heated with a fused mixture of sodium

* See footnote on p. 70.

nitrate and hydroxide in a silver vessel, the metal is oxidised to the trioxide, Ir_2O_3; and on treating the residue with *aqua regia*, a dark-coloured solution is obtained of the double chloride, $2NaCl, IrCl_4$.

This solution may be used for the following reactions :—

When sulphuretted hydrogen is passed into the solution, the brown colour disappears owing to the reduction of the $IrCl_4$ to $IrCl_3$ (or Ir_2Cl_6) and simultaneous precipitation of sulphur. The further passage of the gas throws down the trisulphide, Ir_2S_3, as a dark brownish precipitate.

The double chlorides, $2NH_4Cl, IrCl_4$ and $2KCl, IrCl_4$, are precipitated by the addition of ammonium chloride and potassium chloride respectively. They are both dark brownish-red precipitates, insoluble in strong solutions of the precipitants.

By the action of reducing agents (*e.g.* ferrous or stannous salts, nitrites, etc.), these double chlorides are reduced, giving similar compounds containing the lower chloride of iridium, and having the composition expressed by the formulæ $3NH_4Cl, IrCl_3$ and $3KCl, IrCl_3$ respectively. The solution is at the same time decolorised, and the double chloride gradually deposits. When caustic alkali is added to a solution of iridic chloride (or the double sodium salt), and the mixture heated, the solution assumes a deep blue colour owing to the precipitation of iridic hydroxide, $Ir(HO)_4$, which when separated appears as an indigo-blue powder. This reaction serves to distinguish iridium from platinum.

Tellurium and Selenium.—These two elements belong to the same natural family as sulphur, which in some respects they closely resemble. They both lie on the borderland between the non-metals and the true metals. While selenium forms no stable compounds in which it forms the positive constituent, tellurium exhibits feeble basic properties ; the oxide, TeO_2, being both an acid-forming and a salt-forming oxide.

Both elements form hydrogen compounds corresponding to sulphuretted hydrogen, and closely resembling it in properties. Thus, when compounds of either element are heated on charcoal with sodium carbonate, sodium telluride, Na_2Te, or selenide, Na_2Se, is formed. These are decomposed by acids, with formation of the respective hydrogen compounds, whose odour is even more offensive than that of sulphuretted hydrogen. Or if the sodium compounds are moistened with water upon a silver coin, a black stain is produced of silver telluride or selenide.

Sulphuretted hydrogen gives, with tellurous compounds, a brown precipitate of tellurous sulphide, TeS_2, but with selenious compounds the precipitate consists of selenium and sulphur, selenious sulphide being too unstable to exist. Both precipitates, however, are soluble in ammonium sulphide. With sele*nic* compounds (selenates) sulphuretted hydrogen gives no precipitate until the selenate is reduced to selenite.

Barium chloride, $BaCl_2$, gives, with solutions of selenates, a white precipitate of barium selenate, $BaSeO_4$. This precipitate is

distinguished from barium sulphate in that, when boiled with hydrochloric acid, it is converted into barium selen*ite*, which is soluble.

Sulphurous acid reduces both tellurous and selenious compounds, with precipitation of the element; tellurium being thrown down as a black powder, while selenium is precipitated in the form of the brick-red amorphous variety.

Both elements burn in the air or in oxygen, with a blue flame, giving rise to the dioxide; in the case of selenium, the combustion is accompanied by a smell of putrid horseradish.

Molybdenum.—The compound of this element most commonly met with is ammonium molybdate, $(NH_4)_2MoO_4$.

From a strong aqueous solution of this salt, hydrochloric or nitric acid gives a white precipitate of molybdic acid, H_2MoO_4, soluble in excess of acid.

When sulphuretted hydrogen is passed into an acidulated solution, the solution first assumes a blue colour, which turns green as the dark-brown sulphide is precipitated. The precipitate produced is the trisulphide, MoS_3, analogous to the trioxide. It is soluble in ammonium sulphide (and alkaline sulphides generally), forming thio-molybdates. These, like the corresponding antimony and arsenic compounds, are decomposed by hydrochloric acid, with the reprecipitation of the tri-sulphide.

The reaction by which molybdic acid is most readily identified, is the formation of the yellow precipitate of ammonium phosphomolybdate, by adding sodium phosphate to a nitric acid solution of molybdic acid.

CHAPTER X.

Reactions of the Metals of Group I.

Silver, Lead, Mercury (as *Mercurous* Mercury).

The classification of these three elements into a group is owing to common properties possessed by their chlorides. In most other respects they are greatly dissimilar, and in the "natural" classification of the elements they take their places in three different families.

Silver, Ag.

Dry Reactions.—Compounds of silver, when heated on charcoal with sodium carbonate in the reducing flame, yield metallic silver; which, being non-oxidisable, is not accompanied by any oxide incrustation upon the charcoal. The metal, however, is slightly volatile in the blowpipe flame, and sometimes a faint red-brown incrustation is thus obtained.

The reduced metal may be removed to a watch-glass, dissolved in nitric acid, and precipitated as chloride.

Wet Reactions.—The salts of silver are derived from the monoxide Ag_2O. Of the common salts, the nitrate is readily soluble, the acetate and sulphate sparingly soluble, in water. (The chlorate, nitrite, and fluoride are also soluble. The solubility of the fluoride is noteworthy in view of the insolubility of the other halogen salts.)

A characteristic property exhibited by a number of the silver salts is their readiness to form soluble compounds with ammonia, which are either double salts of silver and ammonium, such as $NH_4NO_3,AgNO_3$, or belong to the class of salts known as *metall-ammonium* compounds, or metallo-amines. Thus, silver nitrate absorbs ammonia gas and yields the compound $AgNO_3,2NH_3$. The same substance is obtained on adding ammonia solution to silver nitrate (a neutral salt) until the precipitate first formed is dissolved.

HCl, and soluble chlorides, give a white amorphous precipitate of silver chloride, AgCl, which, on being warmed or stirred, becomes granulated in appearance, and very quickly settles. On exposure to light, the white compound assumes a slate colour or drab tint, which gradually deepens to a violet, and finally appears brown or black.

Silver chloride is quite insoluble in water, but soluble to a slight extent in strong HCl; dilution causes the complete precipitation. It readily dissolves in ammonia, forming the compound $2AgCl,3NH_3$. Nitric acid decomposes this compound, causing the reprecipitation of AgCl, which is practically insoluble in that acid—

$$2AgCl,3NH_3 + 3HNO_3 = 3NH_4NO_3 + 2AgCl$$

Silver chloride is soluble also in KCy, being first converted into silver cyanide, which dissolves in excess of KCy, forming the double cyanide KCy,AgCy. It also dissolves in sodium thiosulphate, with the formation of a double thiosulphate; thus—

$$AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$$

When boiled with potassium hydroxide, silver chloride is converted into silver oxide (black)—

$$2AgCl + 2KHO = 2KCl + H_2O + Ag_2O$$

Silver chloride melts without decomposition at 451°, and resolidifies to a horny mass (horn silver).

[Reactions with bromides, iodides, and cyanides are described under the respective acids.]

KHO, NaHO, or NH_4HO gives a greyish-black precipitate of silver oxide, Ag_2O. Insoluble in excess of the caustic alkalies, but readily soluble in ammonia. If the silver solution is acid, ammonia gives no precipitate, but forms a soluble double salt (see above).

K_2CO_3 or Na_2CO_3 gives a white precipitate of silver carbonate, Ag_2CO_3. Insoluble in excess of the precipitant; soluble in ammonium carbonate, ammonia, and nitric acid.

H_2S or $(NH_4)_2S$ produces a black precipitate of silver sulphide, Ag_2S. Insoluble in dilute acids, except boiling dilute nitric acid, which converts it into nitrate. The H_2S, which by double decomposition is set free, is acted upon by the nitric acid, with the precipitation of sulphur and evolution of nitric oxide (see Lead reactions, p. 80).

Silver sulphide is insoluble in ammonia, ammonium sulphide, or potassium sulphide.

Reduction of Silver Salts to the Metallic State.—Silver compounds (more especially the ammoniacal solution of silver oxide) are readily reduced with precipitation of metallic silver (which often deposits as a coherent mirror) by certain organic substances, as sugar, tartrates, aldehydes, etc. Many inorganic salts also, which act as reducing agents, precipitate metallic silver from solutions of its salts, *e.g.* ferrous sulphate—

$$3AgNO_3 + 3FeSO_4 = Fe(NO_3)_3 + Fe_2(SO_4)_3 + 3Ag$$

Many metals are capable of reducing silver compounds. Mention may be made of the three metals, zinc, iron, and mercury.

If a strip of zinc be immersed in a solution of silver nitrate, crystals of metallic silver are seen to grow out from the surface of the zinc in the manner of the familiar "lead tree." The reducing action of zinc is often employed in the laboratory to convert precipitated silver chloride into metallic silver. The same action of iron is used in one of the metallurgical processes for the extraction of silver; the reaction in both cases is similar—

$$2AgCl + Zn = ZnCl_2 + 2Ag$$
$$2AgCl + Fe = FeCl_2 + 2Ag$$

Mercury in contact with silver chloride similarly precipitates metallic silver, with formation of mercurous chloride—

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag$$

None of these reductions are made use of in qualitative analysis; the latter reaction, however, with mercury has an important bearing upon the separation of silver from mercurous mercury in the usual course of analysis. The separation of these metals is based upon the solubility of silver chloride in ammonia, mercurous chloride being at the same time converted into the black mercurous ammonium chloride—

(1) $Hg_2Cl_2 + 2NH_4HO = NH_2(Hg_2)Cl + NH_4Cl + 2H_2O$

This *mercurous* compound, however, in the presence of silver chloride and excess of ammonia, passes into the corresponding and more stable *mercuric* salt, NH_2HgCl, while the mercury it thus loses, reduces a portion of the silver chloride; thus—

(2) $NH_2(Hg_2)Cl + 2AgCl = NH_2HgCl + HgCl_2 + 2Ag$ *

(3) $HgCl_2 + 2NH_4HO = NH_2HgCl + NH_4Cl + 2H_2O$

* It is possible, but not probable, that the following reaction goes on simultaneously:—

$$2NH_2(Hg_2)Cl + 2AgCl = 2NH_2HgCl + Hg_2Cl_2 + 2Ag$$

The Hg_2Cl_2, being reconverted by the excess of ammonia into mercurous ammonium chloride, would then be in a position to react upon a fresh proportion of silver chloride, so that the action would be continued until the whole of the silver became reduced; this, however, does not appear to be the case.

The entire change, therefore, may be summed up in the single equation following :—

$$Hg_2Cl_2 + 2AgCl + 4NH_4HO = 2NH_2HgCl + 2NH_4Cl + 4H_2O + 2Ag$$

In the practical separation, therefore, a small quantity of silver, in presence of a large proportion of mercury, might escape detection by being entirely precipitated and left upon the filter along with the mercury compound. It will be evident that if the action of the ammonia be allowed to continue sufficiently long, it would be possible to precipitate the whole of the silver if the quantity of mercury present only slightly exceeded the equivalent proportion.

Lead, Mercury.

The reactions of these metals have already been considered in connection with the metals of Group II., Division 1, pp. 76, 79.

Separation of the Metals of Group I.

The separation of these metals from the other groups, depends upon the insolubility of their chlorides in cold water, and consequently their precipitation by hydrochloric acid. The separation of the metals from each other is based upon—

(1) The solubility of lead chloride in hot water.

(2) The solubility of silver chloride in ammonia.

To the solution add moderately dilute hydrochloric acid drop by drop, until a slight excess beyond what is required for complete precipitation has been added. Gently warm the mixture,* and after again cooling it, filter. The filtrate contains Groups II., III., IV., and V.

The **precipitate,** consisting of $PbCl_2$, AgCl, and Hg_2Cl_2, is thoroughly washed in cold water, and then boiled with water (or washed while in the filter with boiling water) and filtered.

The **filtrate** contains $PbCl_2$, which deposits in white needle-shaped crystals on cooling.

Confirm by special test, *e.g.* the formation of $PbCrO_4$.

The **residue** is treated, while still upon the filter, with a small quantity of ammonia, which dissolves the AgCl, and converts the white Hg_2Cl_2 into black $NH_2(Hg_2)Cl$.†

The solution yields a white precipitate of AgCl upon being acidified with HNO_3.

The black residue may be dissolved in a little *aqua regia*, and (after being nearly neutralised) the mercury precipitated upon metallic copper.

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* See footnote on p. 107.

† For conditions under which this separation is incomplete, see p. 114.

Systematic Separation of the Groups.*

(1) **Separation of Group I.**—By precipitation with hydrochloric acid (p. 115).

The precipitate is thoroughly washed with cold water, and examined by the method on p. 115.

(2) **Separation of Group II.**—The filtrate from Group I. is diluted with water (any precipitation of basic bismuth compounds is to be disregarded, as the subsequent action of SH_2 will convert them into the sulphide), and a *moderately slow* stream of sulphuretted hydrogen passed through. The changes which occur during this precipitation should be carefully watched and noted (see Lead, Mercury, Arsenic reactions). Complete precipitation must be ensured (p. 88. See also Arsenic, p. 93). The precipitate is then treated as described on p. 107.

(3) **Separation of Groups IIIA. and IIIB.**—The filtrate from Group II. is boiled until the sulphuretted hydrogen is entirely expelled. Two or three drops of strong nitric acid are added, and the liquid again boiled for a few minutes, in order to oxidise compounds (*e.g.* iron or chromium) which might have become reduced by the action of sulphuretted hydrogen. The liquid is then carefully evaporated to dryness† in a porcelain dish, and if it shows signs

* It may not be out of place at this point to impress once more upon the student the supreme importance of cleanliness, neatness, and method in analysis. Slipshod and careless work inevitably ends in disappointment and failure. All the utensils (test-tubes, beakers, etc.) must be scrupulously clean, being always rinsed once or twice with distilled water after having been washed. Too much care cannot be paid to securing *complete precipitation* in every separation, or to the *thorough washing* of precipitates. The time spent in securing these results is never lost, whereas the slovenly neglect of these points may, and frequently does, involve a repetition of the analysis, and a corresponding sacrifice of time. A little experience will enable the student to keep two or three operations going on at the same time. Thus, while one precipitate is being washed, another precipitation can be made, and the filtration of this second separation can be carried on simultaneously with the other. While these two are filtering, other tests or special reactions can be made. To do this successfully, however, it must be done methodically, and (especially in cases where the analysis has to be interrupted for a time) the various precipitates and solutions should be labelled. Before making a group separation, it is well to make a preliminary test in a small portion of the solution, and if the group-reagent gives no precipitate, the operation may then be omitted with the bulk of the solution.

† "Carefully evaporate to dryness" does not mean that the student may place a lamp under the dish and go away and leave it. The operation must be watched, and as the liquid becomes more and more concentrated the lamp flame must be lowered. As the residue begins to dry round the edges, he should notice if it shows signs of charring, for if there is no organic compound present it is better to avoid strongly heating the dried residue, as the operation

of charring (owing to the presence of citrates, tartrates, etc.), the residue is cautiously heated until such organic matter is completely decomposed. The residue is moistened with a few drops of strong hydrochloric acid, water is then added, and the mixture boiled. The remaining residue, consisting of silica and carbon, is filtered off.*

A small portion of the solution is next tested for phosphoric acid by means of ammonium molybdate (p. 63). To the main portion of the solution ammonium chloride is added in considerable quantity, and the liquid heated to boiling. Ammonia is carefully added until precipitation is complete.

If phosphoric acid is absent, this precipitate is examined for the metals of Group IIIA. by the method on p. 49.

If phosphoric acid is present, the precipitate is treated as explained on p. 68. The filtrate is then saturated with sulphuretted hydrogen,† gently warmed, and filtered. The precipitate is examined for the metals of Group IIIB. according to the plan on p. 62.

(4) **Separation of Group IV.**—The filtrate from Group IIIB. is boiled briskly, with the addition of a little hydrochloric acid, to decompose ammonium sulphide and expel all the sulphuretted hydrogen. Any precipitated sulphur is removed by filtration. The solution is then rendered alkaline by addition of ammonia, and ammonium carbonate added until precipitation is complete. The solution may be warmed, but must not be boiled (see p. 34). The precipitate is examined for the metals of Group IV., as indicated on p. 35.

(5) **Detection of Metals of Group V.**—The filtrate from Group IV. is tested for magnesium, potassium, and sodium,‡ as described on p. 25.

is likely to render certain oxides (*e.g.* Fe_2O_3, Cr_2O_3, Al_2O_3) very difficult of solution in hydrochloric acid.

* If by a preliminary test upon a small portion of the solution (by evaporating it upon a platinum capsule) it is found that there is no silicious or carbonaceous residue, the main bulk of the liquid need not be evaporated down.

† Or ammonium sulphide may be used for the precipitation (see, in this case, the action of ammonium sulphide on nickel sulphide).

‡ Ammonium obviously cannot be tested for in this solution, since ammonium salts have been frequently introduced during the course of analysis. The test for this "metal" must therefore be made in a portion of the original solution.

APPENDIX TO CHAPTER X.

THE RARE METALS OF GROUP I.

The rare metals of this group are *thallium* and *tungsten*.

The compounds that are precipitated by the group-reagent being *thallous chloride*, TlCl, and tungstic acid, H_2WO_4, in a hydrated condition.

Thallium.—Two classes of compounds of thallium are known, namely, *thallous* salts (derived from thallous oxide, Tl_2O) and *thallic salts* (derived from thallic oxide, Tl_2O_3). In the thallous compounds (which are the more stable of the two classes), the element shows a resemblance to the alkali metals on the one hand, and to lead on the other. For example, thallous hydroxide, TlHO, is soluble in water, giving a strongly alkaline solution; hence KHO, NaHO, and NH_4HO give no precipitate with *thallous* solutions. Thallous carbonate, Tl_2CO_3 is moderately soluble in water, and therefore is only precipitated by carbonates of the alkalies from concentrated solutions (compare *Thallic* salts). Again, platinic chloride gives with thallous solutions an orange-yellow precipitate of thallous platinic chloride, $2TlCl,PtCl_4$. On the other hand, its resemblance to lead is specially seen in the chloride, iodide, and chromate.

Hydrochloric acid (or soluble chlorides) gives a white curdy precipitate of TlCl. Like lead chloride it is slightly soluble in cold water, and dissolves more readily in hot water (100 parts of water at 16° dissolve 0·265 parts, while at 100° 1·427 parts are dissolved).

It is at once distinguished from lead chloride by the fact that it is readily soluble in strong sulphuric acid, forming soluble thallous sulphate. It is distinguished from silver chloride in not being soluble in ammonia, and in not changing colour on exposure to light. Potassium iodide gives a bright golden-yellow precipitate of thallous iodide, TlI; while potassium chromate throws down thallous chromate, Tl_2CrO_4, also (like the lead compound) yellow in colour.

Thallous sulphide (black) is readily soluble in mineral acids; hence sulphuretted hydrogen only gives complete precipitation in acetic acid solutions (or in alkaline solutions). With ammonium sulphide precipitation is complete, but the precipitate rapidly undergoes atmospheric oxidation into the sulphate, which passes into solution. Thallic salts are readily distinguished from thallous compounds. Thus the chloride, $TlCl_3$, is soluble in water; hence hydrochloric acid gives no precipitate. Potassium chromate, similarly, gives no precipitate. With potassium iodide, a mixture of *thallous* iodide and iodine is precipitated, while with sulphuretted hydrogen the compound is reduced to the thallous state, with precipitation of sulphur.

The caustic alkalies, and also the alkaline carbonates, give a brown precipitate with *thallic* solutions, consisting of an oxy-hydroxide, TlO(HO).

Thallium, like lead, is easily reduced from solutions of its salts by metallic zinc, the thallium being deposited upon the zinc in a spongy metallic state.

When introduced into a Bunsen flame upon a platinum wire, thallium salts impart a characteristic brilliant green colour, which, when viewed through a spectroscope, is seen to consist of one bright green line.

Tungsten.—The compound of this element most commonly met with in commerce is sodium tungstate. The formula representing the composition of the *normal* salt is $Na_2WO_4 2H_2O$.* The tungstates of the alkalies are alone soluble.† Hydrochloric acid gives a white precipitate of hydrated tungstic acid. When air-dried, this precipitate has the composition $WO(HO)_4$, or H_2WO_4, H_2O. When dried over sulphuric acid, it loses H_2O and is converted into the normal acid. The precipitate is insoluble in excess of acid.

The most characteristic reaction for compounds of tungsten is the blue colour given when either metallic zinc or tin or stannous chloride is added to a solution of a tungstate, and the solution strongly acidified with hydrochloric acid. On the addition of stannous chloride a pale yellow precipitate is produced, which, on the addition of hydrochloric acid and gently warming, turns deep blue.‡

Sulphuretted hydrogen gives no precipitate in acid solutions, but causes the solution to assume a blue colour.‡

Tungsten trisulphide, WS_3, is a thio-anhydride, forming soluble thio-tungstates with alkaline sulphides; hence, ammonium sulphide gives no precipitate with solutions of alkaline tungstates. But on acidulating the mixture with hydrochloric acid, the sulphide is thrown down as a dark brown precipitate.

* There is quite a number of sodium tungstates, which may all be regarded as compounds of the normal salt with varying quantities of the trioxide. Of these the so-called *metatungstate* and *paratungstate* are articles of commerce—

Sodium metatungstate, $Na_2W_4O_{13}, 10H_2O$; or $Na_2WO_4, 3WO_3, 10H_2O$
Sodium paratungstate, $Na_{10}W_{12}O_{41}, 21(\text{or } 28)H_2O$;
or $5Na_2WO_4, 7WO_3, 21(\text{or } 28)H_2O$

The former of these two salts is the common compound sometimes used for rendering fabrics uninflammable.

† The oxides of tungsten are all *acidic* in their characters, and no salts of this element are known in which it functions as the positive or basic constituent.

‡ The blue colour is believed to be due to the formation of a lower hydrated oxide.

CHAPTER XI.

The Non-metals and their Acids.

One of the chief chemical distinctions between metals and non-metals is that, while the oxides of the former exhibit, generally speaking, *basic* properties, the latter elements give oxides which are *acidic* in their character. Two exceptions to this generalisation respecting the non-metals are seen in the case of hydrogen (whose oxides are not acidic), and the element oxygen itself. Although the number of non-metals is comparatively very small, the number of acids derived from them is very considerable, owing to the fact that many of these elements give rise to several acids.

All the elements belonging to this section form compounds with hydrogen; but only in the case of *fluorine*, *chlorine*, *bromine*, *iodine*, and *sulphur* are the hydrogen compounds included among the acids in analytical classification.

The classification of the acids (or acid radicals) is based, as in the case of the metals, upon the solubility or insolubility of certain of their salts produced by interaction with certain specified reagents. They are in this way divided into certain arbitrary groups, but the mode of treatment differs entirely from that adopted in the case of the metals. The reagents referred to are not employed as "group-reagents" to separate one group of acid radicals from another; but each acid is separately detected by a special test. The use of the general reagent is in order to ascertain by a single operation the absence, or otherwise, of an entire group, whereby the necessity for applying a number of separate tests may be obviated.

The study of the special reactions for the non-metals and their acids may therefore be made irrespective of their analytical classification, and it will be more advantageous to postpone the consideration of the classification until a knowledge of the special reactions has been gained, and the student is prepared to undertake the systematic detection of the acids.

The non-metals and their acids which will be included in this section are the following :—

Chlorine : hydrochloric acid, hypochlorous acid, chloric acid, perchloric acid.

Bromine : hydrobromic acid, bromic acid.

Iodine : hydriodic acid, Iodic acid.

Fluorine : hydrofluoric acid, hydrofluo-silicic acid.

Sulphur : sulphuretted hydrogen, sulphuric acid, sulphurous acid, thio-sulphuric acid.

Nitrogen : nitric acid, nitrous acid.

Phosphorus : phosphoric acid, phosphorous acid, hypophosphorous acid.

Carbon : carbonic acid, formic acid, oxalic acid, acetic acid, tartaric acid, citric acid, cyanogen, hydrocyanic acid, ferrocyanic acid, ferricyanic acid, cyanic acid, thiocyanic acid.

Silicon : silicic acid.

Boron : boric acid.

In some instances the properties of the elements themselves, in the elemental state, are made use of in analysis ; such, for instance, as in the cases of chlorine, bromine, and iodine. When this is the case, those properties of the elements by means of which they are most readily identified will be studied. With others, such as fluorine, silicon, boron, the properties of the isolated elements have no analytical bearing, and therefore all description of such elements will be omitted.*

Certain acids, such as arsenious, arsenic, chromic, have already been discussed under their respective metals.

The Halogens.

These elements not only form oxy-acids, but they also combine with hydrogen and yield acids. The salts of these hydrogen acids, *e.g.* chlorides, bromides, and iodides are known as the *haloid* salts, or sometimes as the *halides*.

Chlorine.

The properties by which this element is identified are the following :—

It is a pale greenish-yellow gas, having a characteristic suffocating smell, irritating and rapidly attacking the mucous membrane of the nose and throat. It dissolves in water, imparting its own

* It is presupposed that the student of analysis has already become familiar with the common properties of the non-metallic elements ; and if he has not, they must be sought in text-books of general chemistry.

colour to the solution. It combines readily with many metals; it is a powerful oxidising agent; it liberates bromine and iodine from bromides and iodides respectively; it possesses powerful bleaching properties.

The Liberation of Chlorine from its Compounds.—The method usually resorted to in analysis for the liberation of chlorine, depends upon the action of peroxides (manganese dioxide being employed) upon the hydrogen acid, or upon a chloride in the presence of sulphuric acid—

$$2NaCl + 2H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

For this purpose the mixture of the chloride with sulphuric acid and manganese dioxide is gently warmed in a small flask or test-tube, fitted with a delivery tube, and the evolved gas is allowed to pass into water contained in a second test-tube. As the solution of the chlorine by water is not complete, the characteristic smell of that which escapes solution may be noted, and its bleaching action can be seen by introducing a strip of litmus paper into the mouth of the tube.

The presence of the free chlorine in the water may be detected by the following more delicate tests :—

(*a*) On adding a few drops of the chlorine water to a solution of potassium iodide, to which a little dilute starch paste has been added, a deep blue coloration results, owing to the liberated iodine (set free by the chlorine) uniting with the starch.

(*b*) A crystal of ferrous ammonium sulphate* [$FeSO_4,(NH_4)_2SO_4,6H_2O$] is dissolved in water, and a few drops of ammonium thiocyanate added. To this colourless mixture a drop or two of the chlorine water is added. This at once oxidises the ferrous salt to the ferric state, which, in the presence of the thiocyanate, immediately gives rise to the wine-red coloration due to ferric thiocyanate.

Hydrochloric Acid and Chlorides.

Hydrochloric acid is a colourless gas having a sharp choking smell. It fumes in contact with moist air, is strongly acid, but has no bleaching properties. It is extremely soluble in water, the solution constituting the ordinary reagent.

Hydrochloric acid is liberated in the gaseous state when

* This double salt is used instead of ferrous sulphate, as it is less easily oxidised by the air, and therefore is more easily obtained free from ferric compounds.

chlorides (except those of tin, lead, mercury, and silver) are gently heated with strong sulphuric acid—

$$KCl + H_2SO_4 = HKSO_4 + HCl$$

The presence of free hydrochloric acid in a solution containing a soluble chloride may be detected by gently warming the liquid with manganese dioxide (without the addition of sulphuric acid); chlorine is evolved, which may be detected by the methods already described—

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$$

Chlorides are all soluble in water, except those of the metals of Group I. ($PbCl_2$ being soluble in hot water), and certain others which are decomposed by water. The chief of these latter salts are the chlorides of (phosphorus, arsenic), antimony, bismuth, and tin. In contact with water these give either an oxide or an oxychloride of the metal, with formation of free hydrochloric acid (see Reactions of these metals).

Silver nitrate, $AgNO_3$, gives, in solution of chlorides or hydrochloric acid, a white precipitate of silver chloride. Insoluble in nitric acid. Readily soluble in ammonia, even dilute (for further properties, see Silver reactions, p. 113).

AgCl is distinguished from either AgBr or AgI by the fact that chlorine water is without action upon it (see *Bromides and iodides*). It may also be distinguished in the following way :—

Reduction by Zinc.—If the washed precipitate of AgCl be mixed with a little very dilute sulphuric acid, and a strip of zinc placed in the mixture, the silver chloride turns grey, owing to its reduction to metallic silver, while zinc chloride passes into solution. This, on treatment with manganese dioxide and sulphuric acid, will yield chlorine.

Fusion with sodium carbonate converts AgCl into metallic silver and sodium chloride. On treatment with water, chlorine can be liberated from the solution, as in the foregoing.

Formation of Chromyl Chloride.—When a chloride is mixed with potassium dichromate (the two salts being powdered together), and the mixture gently warmed with strong sulphuric acid, a red-brown vapour is disengaged (resembling bromine in colour, but very different in smell) consisting of chromyl chloride, CrO_2Cl_2—

$$4KCl + K_2Cr_2O_7 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 2CrO_2Cl_2 *$$

* We may regard this action as taking place between chromium trioxide (formed by the action of the sulphuric acid upon the dichromate) and hydrochloric acid (from the interaction of the chloride and sulphuric acid); thus—

$$CrO_3 + 2HCl = H_2O + CrO_2Cl_2$$

The gas is decomposed by water or alkaline hydroxides, forming in the latter case an alkaline chromate and chloride; thus—

$$CrO_2Cl_2 + 4NH_4HO = (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O$$

If the reaction be made in a test-tube or small flask fitted with a delivery tube, and the vapour of the chromyl chloride (which is a deep red fuming liquid at ordinary temperatures) be passed into a second test-tube containing ammonia, the above decomposition takes place. The presence of ammonium chromate is seen by the yellow colour which the liquid assumes, and the presence of the chromate is proof of the presence of a *chloride* in the first test-tube or flask. [The presence of the [illegible] may be [illegible] confirmed by applying a special test, s[illegible] reacti[illegible] ydrogen peroxide.]

By means of this test i[illegible] detect a chloride *in the presence of* either a bro[illegible] neither bromine nor iodine form similar chromyl co[illegible] a bromide or iodide is treated in this way, bromin[illegible] apour escapes alone.

Bromine.

Bromi[illegible] vn-red, volatile liquid, which passes into a brown-r[illegible] t ordinary temperatures. It has a powerful, irritating sm[illegible] ks the mucous membrane of the nose and throat, and causes the eyes to smart. It bleaches, but less easily than chlorine. It produces a yellow colour with starch. It dissolves in water, giving a reddish solution (*bromine water*), and is soluble in ether and in carbon disulphide, giving reddish-brown solutions.

Liberation from its Compounds.—Bromine is liberated from bromides by the action of manganese dioxide and sulphuric acid (compare chlorine). The solution of the bromide and the manganese dioxide are placed in a small beaker, and a little strong

It is important to bear in mind that with an excess of hydrochloric acid (which would result if the proportion of potassium dichromate to the chloride in the mixture was small) the reaction takes a different course, and *only chlorine is evolved*, the chromium being completely reduced to chromic chloride; thus—

$$CrO_3 + 6HCl = 3H_2O + CrCl_3 + 3Cl$$

Or, to give the complete equation—

$$6KCl + K_2Cr_2O_7 + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Cl_2$$

Hence, in applying this test, it is necessary to employ an excess of the dichromate.

* The former tests (p. 123), which enable one to *distinguish between* a chloride, bromide, and iodide, will not be confounded with a test such as the above, which permits of the detection of one class of salts *in the presence of* others.

sulphuric acid is added. The beaker is then covered over with a piece of moistened blotting-paper upon which a little starch flour has been dusted. The liberated bromine produces a yellow colour with the starch.

Bromine may be liberated by means of chlorine—

starch
$$2KBr + Cl_2 = 2KCl + Br_2$$

of Bromine. A small quantity of carbon disulphide is added to the solution of the bromide in a narrow test-tube; a few drops of chlorine water are added, and the mixture shaken. The liberated bromine is dissolved by the carbon disulphide, giving a red or brownish coloured liquid (according to the amount of bromine), which settles to the bottom of the test-tube. The test must be made with a little care, an excess of chlorine being avoided, as otherwise chloride of bromine is formed, which, being colourless, destroys the test.

Hydrobromic Acid and Bromides.

Gaseous hydrobromic acid closely resembles hydrochloric acid. The properties of the gas are not used in analysis.

The detection of free hydrobromic acid in solution in presence of bromides may be accomplished by gently warming the liquid with manganese dioxide, without the addition of sulphuric acid. Bromine is liberated from the free acid (not from the bromide), and may be detected by the starch reaction given above.

All bromides are soluble in water, except mercurous bromide and silver bromide; lead bromide dissolves in boiling water less easily than the chloride.

Bromides (except Hg_2Br_2 and AgBr), when acted upon by strong sulphuric acid, evolve hydrobromic acid, bromine, and sulphur dioxide (contrast chlorides, which under these circumstances give only HCl), the hydrobromic acid first formed being immediately acted upon by the sulphuric acid; thus—

$$KBr + H_2SO_4 = HBr + HKSO_4$$
$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$

Silver Nitrate, $AgNO_3$, precipitates from solutions of bromides or hydrobromic acid, pale-yellow silver bromide, AgBr (the colour is indistinguishable from white by gaslight). It is insoluble in nitric acid, and difficultly soluble in ammonia (scarcely soluble in dilute ammonia. Contrast AgCl).

AgBr may be distinguished from AgCl by shaking up a little of the washed precipitate with a few drops of carbon disulphide and chlorine water.

Silver bromide is decomposed by metallic zinc in the presence of dilute sulphuric acid, in the same manner as the chloride. Zinc bromide goes into solution, from which the bromine can be separated by either of the methods given under *bromine*.

Prolonged boiling with a strong solu[tion] of sodium carbonate (or, better, heating the dry substances [with] amyl chlor[ide] in a glass tube) decomposes silver bromide. On filter[ing] (at ordinary temperatures) be[low] extraction with water in the case of the *dry* reaction), th[e] above [re]s solution containing sodium bromide may be tested as above.

A bromide may be detected *in the presence* of a chloride by means of chlorine water, which liberates bromine from the bromide, but obviously is without action upon the chloride.

Iodine.

Iodine is a steel-black, shining, crystalline solid. When gently heated it melts and passes into vapour, which has a characteristic deep violet colour. Iodine is very slightly soluble in water, but readily dissolves in water holding hydriodic acid or alkaline iodides in solution, giving a brown liquid. It dissolves in carbon disulphide (also in chloroform), yielding a violet solution. In contact with starch it produces an intense indigo-blue colour, which constitutes one of its most delicate tests.

Liberation of Iodine from its Compounds.—Iodine is more easily set free from combination than either bromine or chlorine, and the methods which are applicable for the liberation of these apply also in the case of iodine. Thus, manganese dioxide and dilute sulphuric acid decompose iodides in a manner precisely similar to that explained on p. 122 for chlorides. Strong acids, as nitric and sulphuric, also expel iodine from iodides, with evolution of oxide of nitrogen, or sulphur dioxide ; *e.g.*—

$$2KI + 2H_2SO_4 = K_2SO_4 + 2H_2O + SO_2 + I_2$$

The comparative ease with which iodine is liberated from combination, affords the basis of most of the tests by which this element is detected. The following are the reactions most used in analysis:—

1. **Chlorine water,** when added to a solution of an iodide, expels the iodine. The test may be applied as described under bromine, the carbon disulphide in this case being coloured violet.

The presence of the liberated iodine may also be recognised by means of starch. A small quantity of starch paste * is mixed with

* Starch paste is made by mixing a little starch flour into a thin cream with the least quantity of cold water, and then pouring *boiling* water upon it until the dead-white appearance of the starch is changed to a translucent appearance.

the solution of the iodide, and one or two drops of chlorine water added, when the deep indigo-blue compound of iodine with starch is produced. On the addition of an excess of chlorine, the colour is destroyed. Boiling the liquid also destroys the compound, hence, when small quantities of iodine are being tested, it is necessary to avoid using the starch while hot.

Detection of Bromides and Iodides in Solution together.—Although chlorine water liberates both bromine and iodine, the reaction may be employed to detect *both* halogens in the same solution, owing to the fact that the chlorine exerts a *selective* action, expelling first the iodine, and afterwards the bromine. The test is applied in the following way: Carbon disulphide is added to the mixed solution of iodide and bromide in a test-tube, and chlorine water added in *small* quantities at a time, with agitation. If this be done carefully, it is not difficult to see when the further addition of a drop of chlorine water produces no further precipitation of iodine. At this point the carbon disulphide (coloured deep violet with dissolved iodine) is removed from the aqueous liquor either by decanting the latter, or, better, by withdrawing a portion of it by means of a small pipette and transferring it to another test-tube. A fresh quantity of carbon disulphide is now added to this, and a few drops of chlorine water. If the whole of the iodine had been liberated in the first tube, the bromine now begins to be expelled, and the carbon disulphide becomes brown. If a small quantity of iodine were still left, the first drop of chlorine water causes its liberation, and, on shaking, the disulphide will show a pale violet colour. A few more drops of chlorine water, however, will destroy this, and afterwards liberate the bromine.*

2. **Nitrous Acid.**—When a solution of an iodide is acidified (preferably with dilute sulphuric acid), and a few drops of a solution of sodium nitrite added, the nitrous acid generated (by the action of the acid upon the nitrite) decomposes the iodide, with the liberation of iodine. The action is in reality between the nitrous acid and hydriodic acid; thus—

$$HNO_2 + HI = H_2O + NO + I$$

or, to state the complete change—

$$NaNO_2 + 2H_2SO_4 + KI = HNaSO_4 + HKSO_4 + H_2O + NO + I$$

* When the quantity of iodide present is *very small* in proportion to the bromide, it is not necessary to change the carbon disulphide as here described. The chlorine, after liberating the iodine, next begins to combine with it, forming iodine trichloride (therefore destroying the violet colour of the carbon disulphide solution), and afterwards to liberate the bromine. But, if the proportion of iodine present is at all considerable, the yellow colour which the iodine chloride itself imparts to the carbon disulphide—if present in any quantity—renders it practically impossible to distinguish the brownish colour which would be given by moderate quantities of bromine.

Neither bromine nor chlorine is liberated by nitrous acid, hence this reaction allows of the separation of iodine from bromides and chlorides, and therefore the subsequent detection of bromine or chlorine in mixtures of the three salts.

Detection of Iodides, Bromides, and Chlorides in Solution together.—The solution containing the three salts, to which a little carbon disulphide has been added, is acidified with two or three drops of dilute sulphuric acid, and a dilute solution of sodium nitrite added drop by drop until the whole of the iodine has been expelled. On shaking the mixture this will be dissolved by the carbon disulphide, giving the violet solution. The aqueous liquid is then withdrawn with a pipette and divided into two portions. The first is neutralised by the cautious addition of ammonia drop by drop. It is then shaken with chlorine water and carbon disulphide. The bromine is thereby liberated, and imparts its brownish colour to the disulphide. The second portion is evaporated down, mixed with potassium dichromate and sulphuric acid, and the chromyl-chloride test made as described on p. 123.

3. **Ferric Chloride.**—When ferric chloride, acid with hydrochloric acid, is added to a solution of an iodide and the mixture heated, the iron salt is reduced to the ferrous condition, and iodine escapes as a violet vapour—

$$FeCl_3 + KI = KCl + FeCl_2 + I$$

Hydriodic Acid and Iodides.

Gaseous hydriodic acid resembles hydrobromic and hydrochloric acids, except that it is more easily decomposed, being dissociated into iodine and hydrogen by very moderate heat. The properties of the gas are not used in analysis.

All iodides are soluble in water, except those of silver, AgI; mercury, Hg_2I_2 and HgI_2; copper, Cu_2I_2; gold, AuI_3; platinum, PtI_4; palladium, PdI_2; (BiI_2 and PbI_2 sparingly soluble).

The formation of some of these insoluble salts is utilised in analysis.

Silver nitrate, $AgNO_3$, when added to a solution of hydriodic acid or an iodide, gives a pale-yellow precipitate of silver iodide, AgI, insoluble in nitric acid, and more difficult of solution in ammonia than silver bromide. [In very strong solutions the precipitation is incomplete, owing to the partial solubility of AgI in concentrated solutions of HI or KI. Dilution with water reprecipitates the dissolved compound.]

Silver iodide may be distinguished from the bromide or chloride

by shaking up the precipitate with a little carbon disulphide and chlorine water.

Silver iodide is reduced by metallic zinc in the same way as the bromide and chloride, or it may be decomposed (in common with all the other insoluble iodides) by fusion with sodium carbonate.

Copper sulphate, $CuSO_4$, added to a solution of an iodide, gives a dirty brown precipitate, consisting of cuprous iodide, Cu_2I_2, and free iodine (see Copper reactions, p. 87)—

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$$

Cuprous iodide is a white crystalline compound, insoluble in water and in dilute acids; soluble in ammonia and in sodium thiosulphate.

In the presence of suitable reducing agents, the whole of the iodine may be precipitated as cuprous iodide; and as bromine and chlorine are not precipitated under these conditions, this reaction is made use of as a means of separation.

Separation of Iodine as Cuprous Iodide.—To the solution containing an iodide, bromide, and chloride, copper sulphate is added in excess (*i.e.* in quantity more than sufficient to combine with the whole of the iodine). Sodium thiosulphate is added drop by drop from a pipette until the brown colour (due to the free iodine) disappears, and the precipitate is white. When this is filtered, the liquid will be coloured blue with the excess of copper sulphate, and will contain the bromide and chloride, for which it may be examined by methods already described.

The first action of the sodium thiosulphate is to convert the free iodine into sodium iodide, and to form sodium tetra-thionate—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

and the sodium iodide, then reacting upon copper sulphate in the presence of the thiosulphate, has the whole of its iodine precipitated as Cu_2I_2.

Palladious nitrate, $Pd(NO_3)_2$, when added to a solution of an iodide, gives a black precipitate of palladious iodide, PdI_2. The reaction is delicate, notwithstanding that the precipitate is soluble to some extent in an excess of potassium iodide. It serves to detect iodides in the presence of chlorides and bromides.

The Halogen Oxyacids.

Hypochlorous Acid and Hypochlorites.

Hypochlorous acid, HClO, is only known in solution in water, as it readily undergoes decomposition. The solution has a pale yellow colour, and a faint smell (familiar in ordinary *chloride of lime*). It also has bleaching properties.

A solution of the free acid may be distinguished from chlorine water (besides from its odour) by shaking it up with a little mercury. With chlorine water white mercurous chloride, Hg_2Cl_2, is formed, while with hypochlorous acid a brownish-coloured oxychloride is produced—

$$2Hg + 2HClO = HgO,HgCl_2 + H_2O$$

All hypochlorites are soluble in water, therefore no precipitation reactions for their detection are possible. The tests employed for their identification are based upon their oxidising action. They are decomposed by even feeble acids (carbonic), with evolution of chlorine, *e.g.*—

$$NaClO + 2HCl = NaCl + H_2O + Cl_2$$
$$Ca(ClO)_2 + CO_2 = CaCO_3 + Cl_2 + O$$

If a few drops of a solution of a hypochlorite be poured upon litmus paper, and the paper exposed to the action of carbon dioxide (by breathing upon it), it will become bleached where it was moistened, by the evolved chlorine.

The evolution of chlorine by the action of dilute acids *distinguishes hypochlorites from chlorides and chlorates.* The addition of silver nitrate to a hypochlorite results in the precipitation of silver chloride, one-third of the silver going into solution as silver chlorate ; thus—

$$(1)\quad NaClO + AgNO_3 = AgClO + NaNO_3$$
$$(2)\quad 3AgClO = AgClO_3 + 2AgCl$$

The commonest salt of hypochlorous acid is bleaching powder, which is a double chloride and hypochlorite of calcium, having the composition Ca(OCl)Cl. When treated with water it splits up into calcium chloride and calcium hypochlorite, and a clear solution made in this way contains the salt $Ca(ClO)_2$—

$$2Ca(ClO)Cl = CaCl_2 + Ca(ClO)_2$$

Chlorates, Bromates, and Iodates.

The three acids, chloric, $HClO_3$, bromic, $HBrO_3$, and iodic, HIO_3, differ in stability in the opposite order to that usually exhibited by compounds of the halogens ; thus, iodic acid is a comparatively stable solid, while chloric acid can only exist in aqueous solutions containing not more than 20 per cent. of the acid. Beyond this strength, or when heated, it decomposes into oxygen, chlorine, and perchloric acid—

$$3HClO_3 = 2O_2 + Cl_2 + HClO_4 + H_2O$$

Bromic acid under the same conditions breaks up into bromine, oxygen, and water; thus—

$$4HBrO_3 = 5O_2 + 2Br_2 + 2H_2O$$

Iodic acid does not give a blue colour with starch, but it readily parts with its oxygen to such reducing agents as sulphuretted hydrogen or sulphur dioxide, with liberation of iodine; thus—

$$2HIO_3 + 5H_2S = 5S + 6H_2O + I_2 *$$

Similarly, hydriodic acid and iodic acid undergo interaction, the whole of the iodine being thrown down—

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

This reaction affords the means of detecting the presence of an iodate when mixed with an iodide. A little starch is added, and a small quantity of acetic acid (this, while liberating the respective iodine acids from their salts, is not able to decompose the iodic acid), when the blue starch coloration is obtained.

The salts of these acids are produced (mixed with the corresponding *halides*) by the direct action of the halogens upon caustic alkalies; thus, in the case of iodine (bromine and chlorine being similar)—

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O$$

Chlorates are all soluble in water.

Bromates.—The silver and mercurous salts are difficult of solution, and may be obtained by precipitation.

Iodates.—Only the iodates of the alkali metals are soluble in water.

The chlorates, bromates, and iodates are all decomposed by heat, yielding either oxygen and the haloid salt (or oxygen, metallic oxide, and free halogen); or, in some cases, leaving both an oxide and halide in the residue—for example—

(1) $AgClO_3 = AgCl + 3O$

(2) $Mg(BrO_3)_2 = MgO + Br_2 + 5O$

(3) $2Pb(BrO_3)_2 = PbO + PbBr_2 + Br_2 + 11O$

When heated with oxidisable substances (*e.g.* charcoal), deflagration of the mixture results.

Hydrochloric acid decomposes chlorates, with the evolution of chlorine and chlorine peroxide—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + 3ClO_2$$

* Owing to this property, if iodic acid is present in a mixture undergoing analysis, iodine will be precipitated in the process of separating Group II. by means of H_2S. By the continued action of the sulphuretted hydrogen, however, the iodine is converted into hydriodic acid, $H_2S + I_2 = S + 2HI$.

(The use of this mixture as an oxidising agent has frequently been referred to.)

Bromates and iodates under the same treatment give bromine and iodine respectively. In the latter case, chloride of iodine is also formed—

$$2KBrO_3 + 2HCl = 2KCl + H_2O + Br_2 + 5O$$
$$KIO_3 + 6HCl = KCl + ICl_3 + Cl_2 + 3H_2O$$

Sulphuric acid decomposes chlorates, with the evolution of chlorine peroxide (a deep-yellow unpleasant-smelling gas), which on very slight elevation of temperature, explodes with violence—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2HKSO_4 + H_2O + 2ClO_2$$

A minute crystal of potassium chlorate, with about three or four drops of strong sulphuric acid, may be heated in a test-tube; sharp detonations will result, characteristic of chlorates. From bromates sulphuric acid liberates bromine. *Dilute* acid first liberates bromic acid, which *gradually* decomposes into HBr and O. As soon as this decomposition sets in, the HBr reacts upon the $HBrO_3$, with liberation of bromine—

$$HBrO_3 + 5HBr = 3H_2O + 3Br_2$$

Dilute sulphuric acid, therefore, liberates bromine *immediately* from a mixture of a bromide and bromate; but only *gradually*, after an interval, from a bromate alone.

Silver nitrate gives with bromates a white precipitate of silver bromate, $AgBrO_3$; soluble in ammonia. It is decomposed by hydrochloric acid, with liberation of bromine (*distinction from all silver halides*). With iodates, silver nitrate precipitates white silver iodate, $AgIO_3$. Difficultly soluble in nitric acid, *readily* dissolved by ammonia (*distinction from* AgI). With chlorates silver nitrate gives no precipitate.*

Hydrogen sodium sulphite added to a solution of an iodate, liberates the whole of the iodine; thus—

$$2NaIO_3 + 5HNaSO_3 = 3HNaSO_4 + 2Na_2SO_4 + H_2O + I_2$$

Similarly, if sulphurous acid be added to the ammoniacal solution of silver iodate, the iodate is entirely reduced, and the iodine thrown out as silver iodide—

$$AgIO_3 + 3H(NH_4)SO_3 = 3H(NH_4)SO_4 + AgI$$

* For method of detecting a chlorate and nitrate in solution together, see Nitric acid (p. 147).

Barium chloride precipitates from soluble iodates, white barium iodate, $Ba(IO_3)_2$. Slightly soluble in water, insoluble on addition of alcohol; slightly soluble in nitric acid, easily soluble in hydrochloric acid. (This reaction affords a means of separating iodic from hydriodic acid, as well as from all other halogen acids.)

A chloride may be separated from a chlorate by adding to the solution silver sulphate. Silver chloride is precipitated, and removed by filtration. Sodium carbonate is then added to remove the excess of silver, and any metals other than the alkalies which might be present; and the solution evaporated to dryness, and heated. The chlorate is thereby converted into chloride.

Perchlorates.

The perchlorates are all soluble in water, and are more stable than the chlorates. Thus, when potassium chlorate is heated, the final products of the decomposition are KCl and O. But as an intermediate product potassium perchlorate is formed; thus—

$$2KClO_3 = KClO_4 + KCl + O_2$$

and on applying a *higher* temperature, the potassium perchlorate is finally resolved into potassium chloride and oxygen. (Bromates, when heated, pass at once into bromides, with evolution of oxygen.)

Sulphuric acid liberates perchloric acid, $HClO_4$, a colourless, fuming, corrosive, volatile liquid. The mixture of the perchlorate and acid does not become yellow; and on warming, the acid distils without decomposition (*distinction from chlorates, also from bromates*).

Hydrochloric acid has no action on perchlorates (*distinction from chlorates, bromates, iodates*).

Fluorine, Hydrofluoric Acid, and Fluorides.

The properties of the element are not made use of in analysis, as fluorine is not liberated by any of the ordinary analytical reactions.

Hydrofluoric acid is a colourless, fuming, highly corrosive liquid, boiling at 19·5° C., therefore extremely volatile. It dissolves in water, and even a moderately dilute solution attacks the skin violently. The most characteristic property of the acid, either gaseous or in solution, is its power of dissolving silica (therefore glass): its application is described below.

Liberation of Hydrofluoric Acid.—Fluorides are decomposed by strong sulphuric acid, with evolution of the acid in the

gaseous condition. Thus with the mineral *cryolite*, and the still commoner *fluor spar*—

$$2Na_3AlF_6 + 6H_2SO_4 = 3Na_2SO_4 + Al_2(SO_4)_3 + 12HF$$
$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

Hydrofluoric acid is also evolved when a fluoride is heated with powdered hydrogen potassium sulphate—

$$CaF_2 + 2HKSO_4 = CaSO_4 + K_2SO_4 + 2HF$$

Certain acid fluorides, when heated alone, decompose with evolution of hydrofluoric acid ; thus—

$$HF,KF = KF + HF$$

The fluorides of the *non-metals* are all volatile without decomposition.

The fluorides of the alkali metals, and of silver, mercury (iron, aluminium, tin), are soluble in water. Those of the alkaline earths, and of lead (copper, zinc, manganese), are insoluble.

Calcium chloride gives a transparent gelatinous precipitate of calcium fluoride, CaF_2, partially soluble in hydrochloric acid.

Barium chloride throws down a white precipitate of barium fluoride, BaF_2, partially soluble in HCl.

Silver nitrate gives no precipitate, as silver fluoride is soluble in water (*distinction between a fluoride and the other halides*).

Formation of Silicon Fluoride.—When hydrofluoric acid comes in contact with silica, or silicates (such as glass), the silicon dioxide is dissolved, and gaseous silicon fluoride is formed—

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The test may be applied in the following ways :—

(*a*) **Etching Glass.**—The powdered fluoride is mixed with strong sulphuric acid in a small dish or tray, made of lead (or a platinum capsule). It is covered with a small piece of sheet glass which has been coated on one side with wax,* and some marks or words scratched upon the wax. In a few minutes the exposed parts of the glass will have become eaten into or dissolved away by the acid gas ; so that, on removing the wax with a little hot water, the marks or letters will be found to be etched into the glass.

(*b*) **The Decomposition of Silicon Fluoride by Water.**—If the fluoride (natural fluoride) contains much silica, or if it be

* A little paraffin wax is melted in a test-tube, and poured upon the previously warmed glass plate. The liquid wax is made to flow all over the surface of the plate, which is then stood up on edge to drain and cool. In this way a thin and uniform film of wax will be obtained.

intentionally mixed with silica (sand), the action of sulphuric acid is to liberate silicon fluoride, a gas which is without action upon glass. The hydrofluoric acid (from the fluoride), being generated in the immediate presence of silica, at once combines with it; thus—

$$2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O^* + SiF_4$$

This gas is at once decomposed by water, with the formation of hydrofluosilicic acid (soluble in water) and the precipitation of gelatinous silicic acid, H_2SiO_3—

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$$

The mixture of the fluoride and sand is gently warmed in a test-tube with a little strong sulphuric acid, and a glass rod with a drop of water upon the end is lowered into the mouth of the tube. The gas, on coming in contact with the water, is decomposed, and a white deposit of silicic acid is formed upon the rod. [The experiment is rendered more delicate by using a piece of narrow glass tube with a drop of water at the end. By means of a piece of rubber pipe attached to the other end of the tube, the drop of water can be *slowly* sucked up the tube, and the gas which is drawn up after it will then deposit a white film of silica upon the wet walls of the tube. The gas must not be drawn into the lungs.] (See also Hydrofluosilicic acid.)

The Formation of Boron Fluoride.—When a fluoride (finely powdered) is mixed with powdered borax, and the mixture moistened with strong sulphuric acid, gaseous boron fluoride, BF_3, is evolved. The action takes place between the hydrofluoric acid and boric acid, which are disengaged by the action of the sulphuric acid upon the respective compounds—

$$B(HO)_3 + 3HF = 3H_2O + BF_3$$

If the mixture be introduced into the edge of a Bunsen flame upon a loop of platinum wire, the flame is tinged a grass-green colour by the escaping boron fluoride.

[The test may be modified by employing hydrogen potassium sulphate instead of sulphuric acid, and heating the mixture of the three salts upon the platinum wire.]

Hydrofluosilicic Acid and Silicofluorides.

This acid is obtained when silicon fluoride is decomposed by water. The gas is made to bubble into water, and the silicic acid separated by filtration.

* The two molecules of H_2O here produced are not liberated as *water*, but are retained by the calcium sulphate in the form of water of hydration; the fully hydrated compound having the composition $CaSO_4,2H_2O$.

The acid and its salts are decomposed by heat—

$$H_2SiF_6 = SiF_4 + 2HF$$
$$BaSiF_6 = SiF_4 + BaF_2$$

The silicofluorides of potassium, sodium, and barium are precipitable salts, being only difficultly soluble in water. The addition of alcohol renders the precipitation complete (see Reactions of metals of Group IV. and V.). Barium silicofluoride is only sparingly soluble in dilute hydrochloric acid, and is therefore precipitated by barium chloride in a hydrochloric acid solution. Barium silicofluoride, however, is distinguished from barium sulphate by dissolving in strong hydrochloric acid (the solution being afterwards diluted to dissolve any barium chloride which may be thrown down by the strong acid); or by the fact that when dried and heated it evolves silicon fluoride, as shown by the above reaction.

The addition of ammonia to hydrofluosilicic acid, or a soluble silicofluoride, gives a white precipitate consisting of gelatinous silicic acid—

$$K_2SiF_6 + 4NH_4HO = 2KF + 4NH_4F + H_2O + H_2SiO_3$$

CHAPTER XII.

Sulphur.

The chief properties made use of in analysis are the following: Sulphur is a pale-yellow, brittle solid. Insoluble in water; easily soluble in carbon disulphide, from which it is deposited on evaporation in amber-coloured rhombic octahedrons.

When heated in a test-tube, it melts and boils off as a brownish-yellow vapour, which condenses to brown drops on the moderately hot parts of the tube (turning yellow when cold), and as a yellow sublimate on the upper and cooler part of the tube (*flowers of sulphur*).

When heated with access of air, either on a platinum capsule or in a glass tube open at both ends, sulphur burns with a pale blue flame, producing sulphur dioxide (of characteristic smell), and leaving no residue. Nitric acid oxidises sulphur into sulphuric acid, with evolution of nitrogen peroxide.

Liberation of sulphur takes place when certain metallic sulphides are heated alone, either in a tube closed at one end, or with partial access of air; *e.g.*—

$$3FeS_2 = Fe_3S_4 + S_2$$
$$3FeS_2 + 5O_2 = Fe_3O_4 + 3SO_2 + 3S$$

Sulphuretted Hydrogen* and Sulphides.

Sulphuretted hydrogen is a colourless gas, easily distinguished from all other gases by its unmistakable odour. It is soluble in water, and imparts its own smell to the liquid. The solution, however, is unstable, undergoing oxidation and depositing sulphur. The gas burns with a flame resembling that of burning sulphur, and yields water and sulphur dioxide.

Liberation of sulphuretted hydrogen takes place when

* Sometimes called *hydrosulphuric acid*; the solution of the gas in water has a feeble acid reaction. It should be remembered that the gas is poisonous.

certain sulphides (see below) are acted upon by acids. The gas may be recognised (1) by its odour ; (2) by its action upon solutions of metallic salts, *e.g.* lead acetate. The reaction is made in a test-tube, and a piece of paper moistened with lead acetate is held over the mouth of the tube. The sulphuretted hydrogen causes a black stain of lead sulphide.

Sulphides of the alkalies and alkaline earths are soluble in water ; all other metallic sulphides are insoluble (see Analytical classification of the metals).

Soluble sulphides are decomposed by dilute acids (HCl or H_2SO_4), with liberation of sulphuretted hydrogen ; in the case of polysulphides, sulphur is also precipitated.*

$$K_2S + 2HCl + Aq = 2KCl + H_2S + Aq$$
$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$$

Insoluble Sulphides.†—The behaviour of these towards acids has already been considered in detail, in studying the separation of the metals. It may be briefly summarised as follows :—

(*a*) Sulphides decomposed by dilute acids (HCl or H_2SO_4), with liberation of sulphuretted hydrogen : namely, ZnS, MnS, FeS.

(*b*) Sulphides unacted upon by dilute acid, but decomposed by hot strong hydrochloric acid with more or less difficulty : Sb_2S_3, PbS, SnS, NiS, CoS.

(*c*) Sulphides unacted upon by strong hydrochloric acid, but decomposed by *aqua regia*, or by a mixture of hydrochloric acid and potassium chlorate ; HgS, As_2S_3, PtS_2, AuS.

The sulphides of class (*b*), when treated with hydrochloric acid in the presence of zinc, or, better, of reduced iron, readily evolve sulphuretted hydrogen.

Oxidising agents, *e.g.* nitric acid, convert many of the sulphides into oxides or sulphates, sulphur being first separated and afterwards oxidised into sulphuric acid.

When a sulphide is added (in small quantities at a time) to a fused mixture of sodium carbonate and potassium nitrate in a platinum crucible, the sulphide is immediately oxidised. After the mass has cooled, and been extracted with water, the aqueous liquid may be tested for a *sulphate*. The sulphides of classes (*a*) and (*b*), when fused upon a piece of platinum foil (or, better, silver) with

* Under certain conditions hydrogen persulphide is formed, without any evolution of sulphuretted hydrogen.

† Aluminium sulphide, Al_2S_3, is not formed in analysis. It is decomposed by water, with the liberation of sulphuretted hydrogen ; thus—

$$Al_2S_3 + 3H_2O = Al_2O_3 + 3H_2S$$

sodium hydroxide, are decomposed, with the formation of sodium sulphide. If a fragment of the fused mass, after cooling, be placed upon a silver coin and moistened with a drop of water, or upon a piece of paper which has been moistened with a solution of lead acetate, in either case a black stain will be produced ; silver sulphide on the coin, and lead sulphide upon the paper.

Most sulphides, when heated in a glass tube open at both ends, and held in a slightly inclined position in order to cause an air-current to pass through the tube, are decomposed, and evolve sulphur dioxide.

Sodium nitroprusside, $Na_2(NO)FeCy_5$,* gives with alkaline sulphides (*but not with an aqueous solution of sulphuretted hydrogen*) a rich reddish-purple colour. One or two drops of the nitroprusside solution are added to the alkaline sulphide (*e.g.* ammonium sulphide) upon a white plate. The colour is destroyed by caustic alkalies, which must therefore be absent when applying the test. (By this test, a soluble sulphide may be detected in the presence of dissolved sulphuretted hydrogen.)

Sulphuric Acid and Sulphates.

Sulphuric acid is an oily, highly corrosive acid liquid. It combines with water with evolution of heat, and is able to abstract the elements of water from many organic compounds. Thus paper, straw, etc., are blackened or charred by the strong acid. This property is made use of in testing for the free acid in the presence of soluble sulphates : a piece of paper is moistened here and there with the solution, and then carefully dried, when it becomes charred where it had been wetted. Or the solution may be mixed with a little white sugar, and evaporated down in a porcelain dish upon a steam-bath, when a charred residue will be left.

Most sulphates are soluble in water. Barium, strontium, calcium, and lead sulphates are insoluble, or nearly so (see Reactions of the various metals). All sulphates (except ferric sulphate) are precipitated by alcohol, being insoluble in that liquid (hence the use of alcohol in rendering the precipitation of the sulphates of lead, calcium, or strontium complete).

Soluble Sulphates.—Barium chloride, $BaCl_2$, gives with sulphuric acid or soluble sulphates, a white precipitate of barium

* This compound is readily obtained by boiling a little solid potassium ferrocyanide with strong nitric acid, diluting with water, and neutralising with sodium carbonate. The salt easily crystallises in deep red crystals. The exact nature of the action of alkaline sulphides upon it is unknown.

sulphate (see *Barium reactions*), insoluble in hydrochloric acid.* The solutions should be dilute, as barium chloride, being insoluble in strong hydrochloric acid, may otherwise be thrown out of solution; the addition of water dissolves it.

Insoluble sulphates may be decomposed by fusion with sodium carbonate, sodium sulphate being formed. The residue is extracted with water, and the aqueous solution tested with barium chloride after being acidified.

When a sulphate is fused with sodium carbonate (which must be free from sulphates as impurities) upon charcoal in the reducing flame, a sulphide of the alkali metal is obtained. If this be placed upon a piece of paper moistened with acetate of lead, and touched with a drop of dilute hydrochloric acid, sulphuretted hydrogen is liberated, and the lead paper stained black.

[This test is only conclusive evidence of a sulphate when other sulphur compounds are proved to be absent.]

Sulphurous Acids and Sulphites.

Sulphurous acid, H_2SO_3, is only known in solution, being produced when sulphur dioxide is passed into water, or when this gas is liberated from combination (as from sulphites) in the presence of water; thus—

(1) In dilute solution, $Na_2SO_3 + 2HCl + Aq = 2NaCl + H_2SO_3 + Aq$

(2) In stronger solution, $Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$

The anhydride, SO_2, is recognised by its characteristic suffocating odour (familiar as "the smell of burning sulphur").

Reducing Action of Sulphurous Acid.—Sulphurous acid easily takes up oxygen, and passes into sulphuric acid, and some of its most important reactions are those in which it thus acts as a reducing agent. Many of these have been referred to under the metals; thus, potassium permanganate is reduced with formation of manganous sulphate—

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O$$

This reaction affords a delicate test for sulphur dioxide. The gas is cautiously decanted (being much heavier than air) into a test-tube containing water slightly tinted with a minute quantity of potassium permanganate. On shaking the gas and water, the pink colour will be destroyed.

* The insolubility of barium sulphate in hydrochloric acid does not distinguish this compound from barium silicofluoride. The latter compound, however, when dried and heated, gives off silicon-fluoride (see p. 136).

Oxidising Action of Sulphurous Acid.—Sulphurous acid is also capable of undergoing reduction, acting therefore towards more powerful reducing agents in the capacity of an *oxidising* substance. Thus, stannous chloride in presence of hydrochloric acid, is oxidised into stannic chloride, the sulphurous acid being reduced to sulphuretted hydrogen. This latter then reacts upon the stannic chloride, with precipitation of stannic sulphide—

$$(1)\ 3SnCl_2 + 6HCl + H_2SO_3 = 3SnCl_4 + 3H_2O + H_2S$$
$$(2)\ SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

Nascent hydrogen,* obtained by the action of hydrochloric acid upon zinc, also reduces sulphurous acid to sulphuretted hydrogen,

$$H_2SO_3 + 3H_2 = 3H_2O + H_2S$$

The test may be made by adding a minute trace of sulphurous acid (or a solution of a sulphite) to a mixture of zinc and hydrochloric acid in a test-tube, and applying acetate of lead paper to the mouth of the tube.

Sulphites.—The only sulphites soluble in water are those of the alkali metals. They are all decomposed by dilute acids, with evolution of sulphur dioxide (see above). Oxidising agents convert them into sulphates.

When heated by themselves, most sulphites are converted into sulphides and sulphates—

$$4K_2SO_3 = K_2S + 3K_2SO_4$$

Those of the alkaline earths leave an oxide, and evolve sulphur dioxide—

$$BaSO_3 = BaO + SO_2$$

Barium chloride gives a white precipitate of barium sulphite, $BaSO_3$, soluble in dilute HCl (*distinction from* $BaSO_4$).

Lead acetate precipitates white lead sulphite, $PbSO_3$. The salt undergoes no change when boiled (contrast Lead thiosulphate).

Silver nitrate gives a white precipitate of silver sulphite, which, on boiling, is converted into black metallic silver—

$$Ag_2SO_3 + H_2O = H_2SO_4 + Ag_2$$

A sulphate and sulphite in solution may be separated by acidulating

* Nascent hydrogen, obtained by the action of sulphurous acid upon zinc *without* any other acid, reduces the sulphurous acid to hyposulphurous (not to be confounded with *thiosulphuric*) acid, an unstable compound which passes into thiosulphuric acid and water; thus—

$$(1)\ H_2SO_3 + H_2 = H_2O + H_2SO_2$$
$$(2)\ 2H_2SO_2 = H_2O + H_2S_2O_3$$

the dilute solution and adding barium chloride. The precipitated sulphate (insoluble in acid) is removed by filtration. To the solution, which now contains barium chloride and sulphurous acid, an oxidising agent, such as chlorine water, is added, when a precipitate of barium sulphate is again thrown down—

$$BaCl_2 + H_2SO_3 + H_2O + Cl_2 = BaSO_4 + 4HCl$$

Thiosulphuric Acid and Thiosulphates.

The acid is unknown in the free state; when liberated from its salts it at once breaks down into water, sulphur dioxide, and sulphur.

Thiosulphates of barium, lead, and silver are sufficiently difficult of solution in water, to be precipitated on the addition of a solution of a thiosulphate to solutions of the respective metals. All others are more easily soluble. They are all decomposed by acids, with precipitation of sulphur and evolution of sulphur dioxide (*this is characteristic, and distinguishes thiosulphates from sulphites, which only give the dioxide without depositing sulphur*).

When heated alone, thiosulphates are converted into sulphates and polysulphides.

Barium chloride precipitates from a moderately strong solution white barium thiosulphate, BaS_2O_3, decomposed by hydrochloric acid; thus—

$$BaS_2O_3 + 2HCl = BaCl_2 + H_2O + SO_2 + S$$

Silver nitrate gives a white precipitate of silver thiosulphate (easily soluble in excess of sodium thiosulphate, forming the double salt, $AgNaS_2O_3$), which quickly changes colour owing to the formation of black silver sulphide (contrast the behaviour of silver sulphite above)—

$$Ag_2S_2O_3 + H_2O = H_2SO_4 + Ag_2S$$

Lead acetate behaves in a similar manner, giving black lead sulphide (contrast lead sulphite).

Thiosulphates are oxidised by chlorine, bromine, and other oxidising agents, in the same manner as the sulphites—

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = 8HCl + 2HNaSO_4$$

and are also reduced by nascent hydrogen, with formation of sulphuretted hydrogen—

$$Na_2S_2O_3 + 2HCl + 4H_2 = 2NaCl + 3H_2O + 2H_2S$$

Separation of the Sulphur Acids.—A solution containing

a sulphide, sulphate, sulphite, and thiosulphate may be examined in the following way :—

(1) The sulphide is first separated as an insoluble metallic sulphide in such a way as to avoid the liberation of any acid, which would decompose the sulphite or thiosulphate. This is done either by shaking up the solution with a little lead carbonate (or cadmium carbonate), or by adding a solution of zinc chloride which has been rendered alkaline with ammonia. The precipitated sulphide is then removed by filtration. Very small traces of sulphuretted hydrogen will produce a distinct coloration in the white carbonate of lead.

(2) Barium chloride is added to the filtrate, which precipitates barium sulphate and sulphite.

(3) The filtrate from this precipitate is acidified with hydrochloric acid and warmed. The thiosulphate is thereby decomposed, with precipitation of sulphur and evolution of sulphur dioxide.

(4) The mixed barium sulphate and barium sulphite is treated with hydrochloric acid. The sulphate is left, and the sulphite dissolves. On filtering and adding chlorine water, the sulphurous acid is oxidised to sulphuric acid, and a precipitate of barium sulphate is produced.

CHAPTER XIII.

Nitrogen and Phosphorus.

The properties of the element nitrogen in its free state are not employed in the analytical examination of its compounds.*

Nitric Acid and Nitrates.

Nitric acid is a fuming corrosive liquid, miscible with water. It readily dissolves most metals, converting them into nitrates or oxides, with evolution of oxides of nitrogen, and in some cases with the formation of ammonia ; *e.g.*—

$$[Sn + 4HNO_3 = H_2SnO_3 + H_2O + 4NO_2] \times 5$$ (see Metastannic acid)

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 4H_2O + 2NO$$

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$4Zn + 9HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_3$$

The reduction of the nitric acid may be regarded as due to the action of nascent hydrogen, which is developed by the first action of the acid upon the metal—

$$2HNO_3 + 3H_2 = 4H_2O + 2NO$$

The extent to which the reduction of the acid will take place depends upon a number of conditions—namely, the particular metal, the strength of acid, the temperature, and the amount of nitrate which is present in the mixture.

* The presence of nitrogen in organic compounds may readily be detected by heating a small quantity of the solid substance in a test-tube with a fragment of the metal sodium (or potassium). Under these circumstances the nitrogen unites with the carbon of the organic compound, forming cyanogen, which, in the presence of the alkali metal, gives a cyanide of the metal. The still hot tube should be plunged into a small quantity of water in a beaker, which immediately breaks it up and allows the cyanide to dissolve, and the excess of sodium to be quietly acted upon by the water. Two or three drops of both ferrous and ferric salts are added, and the liquid then acidified with hydrochloric acid, when *Prussian blue* will be formed.

With magnesium, and under special conditions with zinc also, free hydrogen is evolved by the action of nitric acid.

Nitric acid also oxidises many of the non-metals ; thus sulphur, phosphorus, and iodine, are converted respectively into sulphuric, phosphoric, and iodic acids.

Nitrates are all soluble in water ; their recognition, therefore, is based upon the oxidising reactions of which they, or the nitric acid which they yield, are capable.

Reduction by Ferrous Salts.—When ferrous sulphate is brought into contact with a mixture of a nitrate and strong sulphuric acid, the solution assumes a deep brown colour. Three chemical changes go to make up the reaction: (1) the liberation of nitric acid by the action of sulphuric acid upon the nitrate ; (2) the oxidation of the ferrous to a ferric salt, with elimination of nitric oxide ; and (3) the absorption of the nitric oxide so formed by a further portion of ferrous salt, forming an unstable brown compound having the composition $NO,2FeSO_4$—

(1) $$KNO_3 + H_2SO_4 = HKSO_4 + HNO_3$$

(2) $$2HNO_3 + 6FeSO_4 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

The test is extremely delicate, and is carried out in the following manner. The solution of the nitrate is mixed with about its own volume of strong sulphuric acid in a test-tube, and the mixture cooled. To this a little ferrous sulphate solution is cautiously added, the tube being held in an inclined position, so that the ferrous sulphate shall float upon the denser liquid already in the tube. Where the two liquids meet, the brown colour will be developed. By a gentle movement of the tube, so as to cause a slight admixture of the liquids at the point where they meet, the brown ring will be still more apparent. The coloured compound is decomposed by heat, with evolution of nitric oxide, hence the necessity for making the test with cold solutions.*

Reduction by Sulphurous Acid.—When copper (or mercury) is heated with sulphuric acid in the presence of a nitrate, nitric oxide is evolved, which, in contact with the air, gives red vapours of nitrogen peroxide—

$$3Cu + 4H_2SO_4 + 2KNO_3 = 3CuSO_4 + K_2SO_4 + 4H_2O + 2NO$$

The sulphur dioxide (developed by the action of the acid upon the

* Ferrous chloride in the presence of hydrochloric acid gives a precisely similar result with a nitrate ; nitric oxide is liberated, which is absorbed by the ferrous chloride to a brown liquid—

$$KNO_3 + 3FeCl_2 + 4HCl = 3FeCl_3 + KCl + 2H_2O + NO$$

copper) is oxidised by the nitric acid (simultaneously generated by the action of the acid upon the nitrate) to sulphuric acid ; thus—

$$(1) \qquad Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$
$$(2) \quad 2HNO_3 + 3SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

The nitrate is mixed with a little strong sulphuric acid, and a few fragments of copper foil or turnings are introduced. On boiling the mixture, red fumes of nitrogen peroxide, NO_2, will appear in the tube, which will be more easily seen by looking down through the mouth of the tube.*

A similar reduction takes place, with the liberation of nitric oxide, when sulphur dioxide is generated in presence of a nitrate, from either a sulphite or a thiosulphate, by the action of sulphuric acid.

A small crystal of sodium thiosulphate is added to the solution of a nitrate, and a few drops of strong sulphuric acid added. On gently warming the mixture, brown fumes are seen in the tube.

Reduction by Nascent Hydrogen. (1) *With Formation of Nitrite.*—When a nitrate in solution is exposed to the gentle action of nascent hydrogen—derived by the action of sodium amalgam, zinc amalgam, or copper-zinc couple—the nitrate is reduced to nitrite—

$$KNO_3 + H_2 = H_2O + KNO_2$$

This test is very delicate, and may be carried out as follows: A small piece of zinc foil (or granulated zinc) is placed in the solution of the nitrate in a test-tube, and *one drop* of copper sulphate added (this causes the deposition of a minute quantity of copper upon the zinc, thus creating the "copper-zinc couple"). The mixture is gently boiled for a minute or two. One drop of the liquid (after cooling) is placed upon a piece of potassium-iodide-and-starch paper,† and then touched with a glass rod moistened with dilute sulphuric acid. The paper will be instantly stained blue by the

* The mechanism of this reaction is sometimes explained by supposing that the nitric acid, set free from the nitrate, acts upon the copper according to the familiar equation $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$. But, as a matter of fact, copper *sulphate*, not *nitrate*, is found in solution, the whole of the nitrogen being converted into nitric oxide. Moreover, *charcoal* may be substituted for the copper. If dilute nitric acid be boiled with charcoal no brown fumes are formed, but on the addition of a little sulphuric acid they at once appear, owing to the action of the sulphur dioxide which is evolved from carbon and sulphuric acid.

† Potassium-iodide-and-starch paper is made by dipping ordinary white note paper into moderately thin starch containing a little potassium iodide, and allowing it to dry. It may be preserved indefinitely if kept in a stoppered bottle, and thus obviates the necessity of constantly making a little starch paste. Every student should prepare for himself a stock of the paper.

liberation of iodine and formation of iodide of starch (test for a nitrite).

(2) *With Formation of Ammonia.*—By the prolonged action of the copper-zinc couple ; or by means of nascent hydrogen produced by boiling a solution of caustic soda with zinc, nitrates (and nitrites) are reduced to ammonia—

$$KNO_3 + 4H_2 = KHO + 2H_2O + NH_3$$

A few drops of the solution of a nitrate are added to caustic soda in a test tube, along with a little granulated zinc. On boiling, ammonia is evolved, which may be detected in the usual way.

Indigo.—Nitric acid oxidises indigo blue (C_8H_5NO), converting it into yellow isatin ($C_8H_5NO_2$). A little concentrated sulphuric acid is tinted with a minute quantity of indigo, and a few drops of a solution of a nitrate added. On heating the mixture the blue colour disappears. (The yellow of the isatin is scarcely visible in small quantities, hence the solution appears bleached.)

Nitrates all undergo decomposition when strongly heated. Nitrates of alkali metals and alkaline earths, when gently heated, are reduced to nitrites, with evolution of oxygen.

Ammonium nitrate passes into water and nitrous oxide. Other nitrates, *e.g.* lead nitrate, leave an oxide of the metal, and give off oxygen and nitrogen peroxide.

When heated with oxidisable substances (carbon, sulphur, etc.) the decomposition is propagated with explosive violence. Thus, when nitrates are heated before the blowpipe on charcoal, deflagration of the charcoal takes place.

Nitrates and chlorates, when present together, are examined by being first converted by heat into nitrites and chlorides. If present as salts of metals other than the alkalies, sodium carbonate is added, and the dry mixture heated until the evolution of oxygen is at an end. The residue is extracted with water, and the solution examined for nitrites and chlorides.

If chlorides are originally present as well as nitrates and chlorates, they must be first removed by precipitation with silver sulphate, as explained on p. 133.

Nitrous Acid and Nitrites.

The acid is not known in the pure state. Even when liberated in dilute solutions, it speedily breaks up into nitric acid, nitric oxide and water. Hence when nitrites are decomposed by acids, nitric

oxide is evolved, which, in contact with atmospheric oxygen, passes into the brown gas NO_2 ; thus—

$$6NaNO_2 + 3H_2SO_4 = 3Na_2SO_4 + 2HNO_3 + 2H_2O + 4NO$$

Nitrites are all soluble in water, but the silver salt is sufficiently difficult of solution to be precipitated, on the addition of silver nitrate, to a (not too dilute) solution of a nitrite.

All nitrites are easily decomposed by *dilute* acids in the cold, with evolution of nitric oxide, as shown in the above equation. If the action takes place in the presence of a ferrous salt, the same brown-coloured compound is produced as in the case of a nitrate. [Nitrites therefore give a "brown ring," when dilute sulphuric, or even acetic, acid is used (*distinction from nitrates*).]

Oxidation Reactions.—Nitrous acid and nitrites part with oxygen, and are converted into nitric oxide—

$$2HNO_2 = 2NO + H_2O + O$$

Thus, when a nitrite is acidified with dilute sulphuric acid in the presence of potassium iodide, the nitrous acid first formed oxidises the potassium iodide (or hydriodic acid), setting free the iodine : the liberated iodine is detected by its action upon starch—

$$2KI + H_2O + O = 2KHO + I_2$$

A few drops of a solution of a nitrite are placed upon potassium iodide-and-starch paper, and a single drop of very dilute sulphuric acid added (by means of a glass rod dipped in the acid) when a blue stain at once appears upon the paper. [Or starch emulsion may be added to the solution of the nitrite, then a drop or two of potassium iodide, and lastly a small quantity of acid.]

Sulphuretted hydrogen is similarly oxidised by a nitrite in presence of an acid, with precipitation of sulphur—

$$H_2S + 2HNO_2 = 2H_2O + 2NO + S$$

Nitrites of the alkali metals are decomposed by sulphuretted hydrogen without the addition of an acid, giving alkaline sulphides.

Reduction Reactions. — Nitrous acid, by absorption of oxygen, passes into nitric acid ; it therefore is capable of reducing other compounds, such as chromates, permanganates, mercurous (but not mercuric) salts, and gold compounds. Potassium permanganate (in presence of acid) is converted into manganous salts, the violet colour of the permanganate being destroyed. Gold and mercurous salts are reduced to the respective metals ; thus—

$$Hg_2Cl_2 + H_2O + HNO_2 = HNO_3 + 2HCl + 2Hg$$
$$2AuCl_3 + 3H_2O + 3HNO_2 = 3HNO_3 + 6HCl + 2Au$$

Detection of Nitrites and Nitrates in the Same Solution.—Owing to the ready decomposition of nitrites by dilute acids, they are easily detected in presence of nitrates, either by the liberation of iodine, the oxidation of ferrous salts, or reduction of potassium permanganate. To find a nitrate when nitrites are present is less simple. The dilute solution of the mixed nitrate and nitrite is acidified with three or four drops of dilute sulphuric acid, and a little ferrous sulphate solution (or a small crystal of the salt) is added. The solution at once becomes dark brown (owing to the absorption, by the ferrous salt, of the nitric oxide liberated from the nitrite). It is then heated (but not allowed to boil), with frequent shaking, when nitric oxide is expelled, and the liquid gradually becomes colourless. The mixture is cooled, and one drop more dilute acid added, and a little more ferrous sulphate. (If all the nitrite present has been decomposed, this addition gives no further coloration.) This solution is now poured carefully on to a small quantity of strong sulphuric acid in a test-tube, so as to float upon the acid, and where the liquids meet a "brown ring" will be formed, due to the nitrate present.

Phosphorus.

The property which phosphorus possesses of emitting a feeble luminosity when exposed to the air, either in the solid state or when vaporised, is made use of in analysis for the detection of the element in the free state. The substance, mixed with water, is boiled in a flask with a narrow neck in a dark room. The issuing steam will then appear luminous as it escapes from the flask; and presents the appearance of a lambent pale greenish flame. A piece of paper moistened with silver nitrate, when held over the neck of the flask, will become blackened, owing to the formation of silver phosphide.*

Phosphoric Acid and Phosphates.

Three phosphoric acids (each with its series of phosphates) are known, namely, orthophosphoric acid, H_3PO_4; pyrophosphoric acid, $H_4P_2O_7$; and metaphosphoric acid, HPO_3.

* Phosphorus is a violent poison, and it is practically only in cases of toxicological examination that free phosphorus is sought for. The allotropic form ("red phosphorus") is not poisonous. It is changed by heat into the ordinary variety.

Orthophosphoric acid is tribasic, and hence produces three classes of orthophosphates, by the replacement of one, two, or three of the hydrogen atoms ; *e.g.*—

Ammonium magnesium phosphate, $(NH_4)MgPO_4$.

Hydrogen sodium ammonium phosphate (*microcosmic salt*), $HNa(NH_4)PO_4$.

Dihydrogen sodium phosphate, H_2NaPO_4.

Normal orthophosphates (not containing a volatile base, as NH_4) are not decomposed when heated alone ; those containing one or two hydrogen atoms, or ammonium as the base, are converted into pyro or meta salts (see below). The only orthophosphates which are soluble in water are those of the alkali metals.

Silver nitrate gives a *yellow* precipitate with soluble phosphates, of silver phosphate, Ag_3PO_4, which distinguishes ortho from pyro and meta compounds.

The chief analytical reactions of the orthophosphates have already been considered in Chap. VII., p. 63.

Pyrophosphoric Acid and Pyrophosphates. — When orthophosphoric acid, or a phosphate containing either one hydrogen atom or one ammonium radical, is heated, it loses water, and is converted into pyrophosphoric acid or a salt ; thus—

$$2H_3PO_4 = H_2O + H_4P_2O_7$$
$$2HNa_2PO_4 = H_2O + Na_4P_2O_7$$
$$2NH_4MgPO_4 = H_2O + 2NH_3 + Mg_2P_2O_7$$

Boiling with acids retransforms pyrophosphates into orthophosphates.

Only the pyrophosphates of the alkalies are soluble in water.

Silver nitrate gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$.

Magnesium sulphate precipitates white magnesium pyrophosphate, $Mg_2P_2O_7$, soluble in excess of magnesium sulphate, and not reprecipitated *in the cold* by ammonia (*distinction from orthophosphates*).

Ammonium molybdate gives no precipitate until the "pyro" acid has been changed to "ortho" by the action of the nitric acid present.

Metaphosphoric Acid and Metaphosphates.†—The acid is formed when the "ortho" or "pyro" acids are strongly heated, whereby water is expelled. It is known as *glacial* phosphoric acid—

$$H_3PO_4 = H_2O + HPO_3$$

* Metaphosphoric acid has the curious property of forming a number of salts which may be regarded as polymers of the ordinary salts (see Newth's "Inorganic Chemistry," p. 437).

The reaction is reversible; for when metaphosphoric acid is dissolved in water, it passes back to the ortho acid—slowly in the cold, quickly when boiled.

Silver nitrate gives a white precipitate of silver metaphosphate, $AgPO_3$.

Magnesium sulphate, in presence of ammonium chloride, gives no precipitate (*distinction from "pyro" and "ortho" acids*).

Albumen (white of egg) is coagulated when shaken up with metaphosphoric acid (or metaphosphates acidified with acetic acid) (*distinction from "pyro" and "ortho" acids, which are without action upon albumen*).

Phosphorous Acid and Phosphites.

Phosphorous acid, H_3PO_3, is tribasic, but the most stable salts are those which contain one atom of hydrogen. Thus, trisodium phosphite, Na_3PO_3, is decomposed by water into hydrogen disodium phosphite, HNa_2PO_3. With the exception of phosphites of the alkalies, the salts of this acid are either insoluble in water or dissolve only with difficulty, and may therefore be precipitated by double decomposition; thus, on the addition of barium chloride to a solution of sodium phosphite, barium phosphite, $HBaPO_3$, is thrown down as a white precipitate. Both the acid and its salts are powerful reducing agents; thus, with silver nitrate a white precipitate momentarily forms, which quickly becomes black from reduced silver. Similarly, mercuric compounds are converted first to mercurous and then to metallic mercury. When strongly heated, phosphites decompose, and give off phosphoretted hydrogen.

Hypophosphorous Acid and Hypophosphites.

Hypophosphorous acid, H_3PO_2, is monobasic; its formula may therefore be written $H(H_2PO_2)$. The sodium salt has the composition $Na(H_2PO_2)$, while the barium salt is expressed by the formula $Ba(H_2PO_2)_2$. All the salts are soluble in water, therefore barium chloride gives no precipitate with solutions of hypophosphites (*distinction from phosphites*).

Hypophosphorous acid and its salts are still more powerful reducing agents than phosphites. One characteristic reaction of this nature, which distinguishes hypophosphites from phosphites, is the reduction of copper sulphate to copper hydride, Cu_2H_2.

On adding copper sulphate to an acidulated solution of a hypophosphite, and gently warming the mixture, a precipitate is obtained—at first yellowish-brown, quickly turning to a dark chocolate-brown colour; thus—

$$2H_3PO_2 + 2CuSO_4 + 3H_2O = 2H_3PO_4 + H_2SO_4 + H_2SO_3 + Cu_2H_2$$

This precipitate of cuprous hydride is distinguishable from the red cuprous oxide, not only by its much darker colour, but by the

fact that when treated with strong hydrochloric acid, it evolves hydrogen ; thus—

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2$$

Under the influence of nascent hydrogen from zinc and hydrochloric acid, hypophosphites as well as phosphites give phosphoretted hydrogen, which imparts to the hydrogen, when it is inflamed, the characteristic colour of the phosphorus flame.

Hypophosphorous acid and its salts, when gently heated, give off phosphoretted hydrogen, leaving phosphoric acid—

$$2H_3PO_2 = H_3PO_4 + PH_3$$

CHAPTER XIV.

CARBON, SILICON, BORON.

Carbon.

THE properties of carbon by which it is most readily recognised are (1) its combustibility in air or oxygen, with formation of only carbon dioxide; and (2) its power to withstand the action of chlorine even at high temperatures, which distinguishes it from all metals or black substances.

Carbonic Acid and Carbonates.

Carbonic Acid, H_2CO_3, is an unstable compound only capable of existence in dilute aqueous solution. It is formed when carbon dioxide is dissolved in water, and has a feeble acid reaction. It is capable of dissolving the normal carbonates of the alkaline earths and of magnesium, forming the so-called "acid" carbonates or "bicarbonates" (the pharmaceutical preparation known as *fluid magnesia* is a case in point)—

$$MgCO_3 + H_2CO_3 = H_2Mg(CO_3)_2$$

All normal carbonates are insoluble in water, except those of the alkalies. The "acid" carbonates are all soluble, but on boiling their solutions, they are converted into normal salts, which (except in the case of the alkaline carbonates) are then precipitated; thus—

$$H_2Ca(CO_3)_2 = CaCO_3 + H_2O + CO_2$$

(The formation of boiler incrustations and the "furring" of kettles are due to this decomposition.)

The normal carbonates of the alkalies are by this reaction readily distinguished from the bicarbonates. Thus, on heating a solution of sodium bicarbonate, effervescence rapidly sets in owing to the escape of carbon dioxide—

$$2HNaCO_3 = Na_2CO_3 + H_2O + CO_2$$

These two classes of salts may also be distinguished by the

difference in their behaviour towards certain metallic solutions, *e.g.* magnesium or mercuric salts. Thus—

With **magnesium sulphate** or chloride, normal sodium carbonate gives a white precipitate of a basic carbonate—

$$5MgSO_4 + 5Na_2CO_3 = MgO,4MgCO_3 + 5Na_2SO_4 + CO_2$$

Sodium bicarbonate gives no precipitate with magnesium salts, the reason being that in the presence of the large quantity of carbonic acid set at liberty from the bicarbonate, the magnesium carbonate is redissolved, forming the soluble magnesium bicarbonate.

With **mercuric chloride,** the normal carbonate gives a reddish precipitate of a basic oxide, while the bicarbonate gives no precipitate.

All carbonates are decomposed by dilute hydrochloric acid (and by nearly all acids) with effervescence, due to the rapid escape of carbon dioxide. The gas is identified by its action upon lime-water (or baryta-water).

The test is made by adding a few drops of acid to the carbonate in a test-tube, and decanting the evolved (heavy) gas into a second test-tube containing a little lime-water, $Ca(HO)_2$. On shaking the lime-water with the gas, the liquid becomes milky, owing to the precipitation of calcium carbonate.

The only other gas which gives a white precipitate with lime-water is sulphur dioxide. This is easily distinguished from carbon dioxide by its smell. If the two gases are present together, the sulphur dioxide (recognised by its odour) may be removed by means of potassium permanganate. The two gases (liberated simultaneously by the action of an acid upon a mixture of a carbonate and sulphite) are passed through a little potassium permanganate solution in a test-tube, fitted as shown in Fig. 14. The sulphur dioxide is absorbed (being oxidised by the permanganate into sulphuric acid), and the carbon dioxide passes on, and can be detected by means of lime-water. If the passage of the gases through the permanganate be continued for a few minutes, the colour of the solution becomes entirely destroyed ; and the liquid may then be tested for sulphuric acid in the usual way.

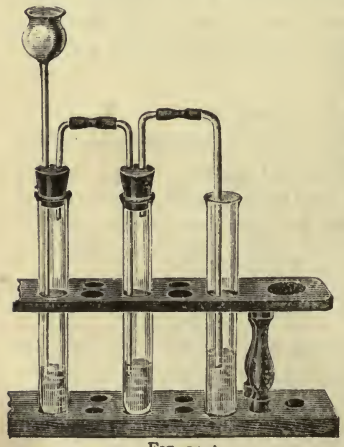

Fig. 14.

When strongly heated, the normal carbonates of the alkali metals (not ammonium) remain unchanged. Those of the alkaline earths are converted at a high temperature into oxides, with evolution of carbon dioxide (illustrated in the process of lime-burning). All other carbonates are more readily decomposed by heat.

Formic Acid and Formates.

Formic acid, H_2CO_2 or H(COHO) (the acid present in ants and in nettles), is a pungent-smelling colourless liquid. The acid is monobasic. All formates are soluble in water. Both the acid and the salts are powerful reducing agents, as one molecule of the acid is capable of withdrawing one atom of oxygen (or its equivalent in chlorine) from compounds capable of reduction. Thus, mercuric chloride is reduced to mercurous chloride, and carbon dioxide is eliminated—

$$2HgCl_2 + H_2CO_2 = CO_2 + 2HCl + Hg_2Cl_2$$

Formic acid and formates are immediately decomposed by concentrated sulphuric acid without the application of heat, into water (absorbed by the acid) and carbon monoxide—

$$H(COHO) = H_2O + CO$$

The escaping carbon monoxide is distinguished by burning with a fine pale-blue flame.

Oxalic Acid and Oxalates.

Oxalic acid, $H_2C_2O_4$, is a white solid, soluble in water, and crystallising from the solution with two molecules of water of crystallisation, $H_2C_2O_4,2H_2O$. The acid is dibasic.

The oxalates of the alkalies are soluble in water, as well as certain acid oxalates (*e.g.* acid oxalate of barium). All other oxalates are insoluble or only sparingly soluble.

Insoluble oxalates are decomposed by mineral acids, with the formation of salts of the mineral acid with the metal contained in the oxalate, and the liberation of oxalic acid. In the case of strong sulphuric acid, the liberated oxalic acid is itself decomposed on the application of a gentle heat ; carbon dioxide and monoxide being disengaged in equal volumes ; thus—

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

the sulphuric acid in this instance, as in the case of formic acid, taking up the elements of water from the molecule.

In the presence of reducible compounds, oxalic acid passes into water and carbon dioxide only, one molecule of the acid taking up

one atom of oxygen. In this way it is able to reduce potassium permanganate, two molecules of which furnish five atoms of oxygen, and therefore oxidise five molecules of oxalic acid ; or one molecule of permanganate causes the liberation of five molecules of carbon dioxide—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$5O + 5H_2C_2O_4 = 5H_2O + 10CO_2$$

Similarly, manganese dioxide, having one atom of available oxygen, when passing to the condition of a manganous salt, is able to oxidise one molecule of oxalic acid ; thus—

$$MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2H_2O + 2CO_2$$

Of the insoluble oxalates, the calcium salt, CaC_2O_4, is of the most importance analytically. Its formation as a special test for calcium has already been considered (p. 33). The precipitate is only slightly soluble in oxalic acid (whereas barium oxalate is somewhat readily dissolved by oxalic acid, forming a soluble acid oxalate), and is scarcely dissolved by acetic acid. It is, however, readily soluble in hydrochloric acid.

When heated, oxalates are all decomposed. Those of the alkalies and alkaline earths are converted into carbonates, with evolution of carbon monoxide. The oxalates of metals which either do not form carbonates, or whose carbonates are decomposed by heat, leave a metallic oxide, and give off carbon dioxide and monoxide either together or in two stages ; thus—

$$(1)\ CaC_2O_4 = CaCO_3 + CO$$
$$(2)\ CaCO_3 = CaO + CO_2$$

In the case of metals whose oxides are decomposed by heat, *e.g.* silver oxalate, the metal is left.

Acetic Acid and Acetates.

Acetic acid, $C_2H_4O_2$ or $H(C_2H_3O_2)$, is a white crystalline solid, which melts at the temperature of a warm room (16° C.). The common reagent is a solution of the acid in water. The acid is monobasic. The acetates are all soluble in water, the silver and mercurous salts being sufficiently difficult of solution to allow of their being precipitated by the addition of moderately strong acetic acid to solutions of the respective metals. Ferric chloride, when added to a solution of an acetate, gives ferric acetate, which is a soluble salt imparting a dark red colour to the solution. When the liquid is boiled, a brownish precipitate separates out, consisting of

basic ferric acetate (p. 69). The acetates are decomposed by mineral acids, acetic acid being liberated; and as acetic acid is volatile without undergoing decomposition, it can be distilled off and recognised by its odour. When an acetate is mixed with strong sulphuric acid and a little alcohol, $(C_2H_5)HO$, and the mixture gently heated, a reaction takes place, resulting in the formation of ethyl acetate (*acetic ether*), a volatile, ethereal, and pleasant-smelling compound.* The mechanism of the reaction is as follows: (1) The sulphuric acid acts upon the alcohol, forming a compound known as sulphethylic acid, $H(C_2H_5)SO_4$; and (2) this then reacts with the acetic acid liberated by the sulphuric acid from the acetate; thus—

$$(1) \quad H_2SO_4 + (C_2H_5)HO = H(C_2H_5)SO_4 + H_2O$$
$$(2) \quad H(C_2H_5)SO_4 + H(C_2H_3O_2) = H_2SO_4 + C_2H_5(C_2H_3O_2)$$

When acetates are heated alone, they blacken slightly, and evolve vapours of a volatile liquid known as acetone. The vapour has a characteristic smell,* and is inflammable.

Tartaric Acid and Tartrates.

Tartaric acid, $H_2(C_4H_4O_6)$, is a white crystalline solid; decomposed by heat, and therefore not volatile. It is soluble in water. The acid is dibasic.

The normal tartrates of the alkalies are freely soluble in water; the "acid" tartrates (especially of potassium and ammonium (see pp. 21 and 23) are sparingly soluble. Other normal tartrates are either insoluble or difficultly soluble, but most of them dissolve in tartaric acid, forming "acid" salts. The tartrates show a great tendency to form soluble double salts with alkalies; thus the tartrates of the metals of Group III. are dissolved by alkalies, owing to the formation of double tartrates. Hence, in the presence of tartaric acid, alkalies fail to give precipitations with solutions of those metals.

Tartrates are decomposed by mineral acids, with elimination of tartaric acid. If heated with strong sulphuric acid, the liberated tartaric acid is broken up into water, carbon dioxide, carbon monoxide, and separation of carbon (*the mixture blackens therefore*); and from the action of the sulphuric acid upon the carbon, sulphur dioxide is formed—

$$H_2(C_4H_4O_6) = 3H_2O + CO_2 + CO + 2C$$
$$C + 2H_2SO_4 = 2H_2O + CO_2 + 2SO_2$$

Calcium hydroxide (lime-water), added to a solution of tartaric acid, gives no precipitate, unless added in sufficient excess

* No description of odours of this kind can convey an exact idea of them. It is therefore only by preparing and smelling the compound, and so actually *learning* its characteristic smell, that the substance can afterwards be recognised by such a test as this.

to ensure the formation of the normal tartrate, which then precipitates out.

Soluble calcium salts (not the sulphate) give the same precipitate when added to solutions of normal tartrates. The precipitate is soluble in tartaric acid, and also in acetic acid (contrast Calcium oxalate).

Silver nitrate gives, with solutions of normal tartrates, a white precipitate of silver tartrate. The precipitate is soluble in ammonia, and on gently warming the ammoniacal solution, the silver is precipitated as a coherent film or mirror upon the glass vessel. The test is made in the following way :—

A small quantity of a normal tartrate (the double tartrate of sodium and potassium, Rochelle salt, is a suitable salt to employ in order to study the reaction), not much larger than a pin's head, is dissolved in a little water in a carefully cleaned test-tube, and a few drops of silver nitrate added. Dilute ammonia is then added drop by drop, until the precipitated silver tartrate is *nearly* wholly dissolved. The mixture is then diluted with water, so as to about half fill the test-tube. The tube is then placed into boiling water for a few minutes, when the silver will be deposited as a brilliant mirror upon the glass. (*This reaction distinguishes tartaric acid from all the other acids treated in this chapter.*)

When heated alone, tartaric acid and tartrates are decomposed, evolving vapours which are inflammable, and emitting a smell resembling that of burnt sugar. The residue, in the case of tartrates of the alkalies and alkaline earths, consists of carbon and the carbonate of the alkali ; while other tartrates leave either a metallic oxide or metal mixed with carbon.

Citric Acid and Citrates.

Citric acid, $H_3(C_6H_5O_7)$, closely resembles tartaric acid in appearance. It is soluble in water. The acid is tribasic.

The citrates of the alkalies are readily soluble ; those of the alkaline earths are less easily soluble ; calcium citrate, however, being soluble in *cold* water, but nearly insoluble in hot water.

Calcium hydroxide, or **calcium chloride,** if moderately dilute, gives no precipitate in the cold, when added to solutions of citric acid or normal citrates. (A *strong* solution of calcium chloride mixed with a *strong* solution of a citrate may give a precipitate even in the cold. With more dilute solutions, the calcium citrate is *gradually* precipitated ; completely only after a few hours) ; but on heating the mixture, a white precipitate of calcium citrate is produced (*distinction from tartaric acid*). The precipitate is soluble in acetic acid (*distinction from calcium oxalate*).

By means of the reaction with calcium chloride, tartaric and citric acids may be detected when mixed together. Calcium chloride is added to the cold and not too concentrated solution, whereby calcium tartrate is precipitated ; on filtering and heating the filtrate, a further precipitation takes place of calcium citrate.

Silver nitrate gives a white precipitate of silver citrate, soluble (like the tartrate) in ammonia; but the ammoniacal solution does not deposit metallic silver when warmed (compare Silver tartrate).

Cyanogen.

Cyanogen, (CN) or Cy, is a negative compound radical, which resembles the halogen elements in many of its chemical habits. It is liberated when the cyanides of many of the heavy metals (*e.g.* mercuric cyanide) are heated alone.

Cyanogen is a colourless gas, with an odour which is like the *taste* of bitter almonds or the kernels of cherry-stones.* It burns with a characteristic flame, having a beautiful mauve-pink colour. The gas is soluble in water, but the solution is unstable. It also dissolves in yellow ammonium sulphide, forming ammonium thiocyanate—

$$(NH_4)_2S_2 + 2Cy = 2NH_4CyS$$

This reaction forms a ready method for the detection of small quantities of cyanogen. The test is made in the following way. A piece of filter-paper, moistened with a drop of yellow ammonium sulphide, is held over the mouth of the test-tube in which the compound is being heated. If the yellow colour of the sulphide is destroyed, the colourless spot is touched with a glass rod dipped in ferric chloride, when a red stain of ferric thiocyanate is at once obtained. If the quantity of cyanogen is so small that the colour of the ammonium sulphide is not destroyed, a single drop of a solution of zinc chloride or sulphate is placed upon it, using a pipette (this removes the excess of ammonium sulphide, forming *white* zinc sulphide), after which the spot is touched with ferric chloride, when the red stain will appear. (Ferric chloride cannot be added until the ammonium sulphide is removed, or a *black* stain of ferrous sulphide will be produced.)

Hydrocyanic Acid and Cyanides.

Hydrocyanic acid, HCN or HCy, is the analogue of the hydrogen acids of the halogens. In the pure state it is a very volatile liquid (B.P., 27° C.). It is liberated when certain cyanides (see below) are decomposed by acids, and may be recognised by

* Cyanogen, and also hydrocyanic acid, are most deadly poisons, and therefore the greatest caution must be exercised in smelling either of these compounds. The odour of the greatly diluted gas seems to be perceived more by the sense of taste than of smell, being recognised as a somewhat bitter but not unpleasant sensation at the back of the throat.

its odour (see footnote, p. 159), or by applying the reaction with ammonium sulphide as described for cyanogen—

$$(NH_4)_2S_2 + HCy = (NH_4)HS + NH_4CyS$$

Single Cyanides.—These are binary compounds, analogous to the chlorides. Of these the cyanides of the alkalies, alkaline earths, and mercuric cyanide are soluble in water (barium cyanide with difficulty); all others are insoluble. The aqueous solutions of these cyanides are unstable, undergoing gradual decomposition; chiefly into a formate and free ammonia—

$$KCN + 2H_2O = K(CHO_2) + NH_3$$

The cyanides of the alkali metals are unchanged when strongly heated alone, while those of the heavy metals are mostly converted into cyanogen * and the metal, or in some cases into nitrogen, carbon, and metal, or a metallic carbide. Under the influence of heat, the cyanides of the alkalies readily take up oxygen or sulphur, from compounds capable of yielding these elements, and pass into cyanate or thiocyanate. Hence potassium cyanide is constantly employed in analysis as a reducing agent in blowpipe reactions.

The alkali cyanides, and some of the insoluble single cyanides (*e.g.* $ZnCy_2$, $PbCy_2$) are readily decomposed by dilute mineral acids; others are only decomposed with difficulty; in either case, with liberation of hydrocyanic acid. They are all decomposed by strong sulphuric acid (some requiring the aid of heat), with formation of metallic sulphates (see p. 164). Mercuric cyanide is decomposed by sulphuretted hydrogen. Cyanides in solution may be detected (1) by the precipitation of insoluble single cyanides by double decomposition (not very characteristic); (2) by the formation of alkali thiocyanate, and subsequently obtaining the red coloration with ferric chloride; (3) by the formation of Prussian blue.

(1) **Silver nitrate,** added to a solution of a soluble cyanide (other than mercuric cyanide), gives a white precipitate of silver cyanide, AgCy; soluble in ammonia, insoluble in nitric acid, and readily soluble in potassium cyanide, giving a double cyanide, KCy,AgCy.

Silver cyanide closely resembles silver chloride; it is, however, readily distinguished by the fact that, when boiled with hydrochloric acid, it is decomposed, with evolution of hydrocyanic acid; and also that, when heated alone, it gives off cyanogen (detected as above), and leaves a black residue of silver and paracyanogen.

* And usually some paracyanogen, a non-volatile black compound, which is a polymeride of cyanogen expressed by the formula $(CN)x$.

(2) **Formation of Alkali Thiocyanate.**—Yellow ammonium sulphide is added to the solution of the cyanide, and the mixture gently boiled for a moment or two. In the case of an alkali cyanide, the following change takes place :—

$$(NH_4)_2S_2 + KCy = KCyS + (NH_4)_2S$$

With mercuric cyanide, the ammonium sulphide precipitates black mercuric sulphide ; thus—

$$HgCy_2 + 2(NH_4)_2S_2 = HgS + (NH_4)_2S + 2NH_4CyS$$

A solution of zinc sulphate is then added (without filtering, in the case of mercuric cyanide), until the excess of ammonium sulphide is removed by precipitation, as white zinc sulphide. The mixture is then filtered, and to the colourless solution a drop of ferric chloride is added, which at once gives the deep red coloration due to ferric thiocyanate. (This test is very delicate.)

(3) **Formation of Prussian Blue.**—To the solution containing the soluble cyanide (or hydrocyanic acid) a small quantity of sodium or potassium hydroxide is added, after which three or four drops both of a ferrous and ferric salt (ferrous sulphate and ferric chloride). The *visible* result is the production of a dirty brown precipitate of the mixed ferrous and ferric hydroxides. The *invisible* result is the formation of ferrocyanide in the solution. The ferrous sulphate, interacting with the cyanide present, forms (1) ferrous cyanide, $FeCy_2$, which in its turn dissolves in the excess of the cyanide, forming the ferrocyanide ; thus, with potassium cyanide—

$$(1)\ FeSO_4 + 2KCy = K_2SO_4 + FeCy_2$$
$$(2)\ FeCy_2 + 4KCy = K_4(FeCy_6)$$

On the addition of hydrochloric acid to the mixture, the precipitated iron hydroxides are dissolved, and the ferric chloride thus formed interacts with the potassium ferrocyanide present, giving rise to the precipitation of ferric ferrocyanide, or, in cases when the amount of cyanide is very small, to a blue or green coloration.

Double Cyanides.—Most of the single cyanides are soluble in alkali cyanides, giving rise to double cyanides. Some of these have an alkaline reaction, are easily decomposed by dilute mineral acids with evolution of hydrocyanic acid, and (like the single cyanides) are poisonous. Others, on the contrary, have a neutral reaction, do not give off hydrocyanic acid when treated with dilute acids, and are not poisonous. The double cyanides are therefore divided into two classes, namely (1) those which are easily decomposed by acids, and (2) those which are decomposed with difficulty.

All double cyanides, like all single cyanides, are decomposed by strong sulphuric acid, and also by fusion with potassium nitrate (or a mixture of ammonium nitrate and sulphate).

(1) **Easily decomposed Double Cyanides.**—From an analytical point of view, these may all be regarded as mixtures of the single cyanide with the solvent cyanide (usually potassium cyanide). Thus, the double cyanides obtained by dissolving the cyanides of zinc, silver, nickel, in potassium cyanide, are expressed by the formulæ $2KCy,ZnCy_2$, $KCy,AgCy$, $2KCy,NiCy_2$.

Their chemical behaviour is practically the same as would be shown by mixtures of potassium cyanide and the several simple metallic cyanides. Thus, when such double cyanides are heated, the alkali cyanide (which is stable at high temperature) remains, and the other portion of the molecule behaves exactly as the single cyanide; *e.g.* the silver cyanide evolves cyanogen, leaving a black residue of silver and paracyanogen.

When treated with acids, the same thing is observed; the alkali cyanide is decomposed with evolution of hydrocyanic acid (just as it would if alone), while the other cyanide in the molecule behaves exactly as though *it* were alone. If it is not one which is decomposed by the acid, it remains; reprecipitated of course, since the solvent cyanide has been decomposed. Thus, the double potassium nickel cyanide, when acted upon by acids, evolves hydrocyanic acid, and the single nickel cyanide is reprecipitated—

$$2KCy,NiCy_2 + 2HCl = 2KCl + 2HCy + NiCy_2$$

In the case of the double potassium zinc cyanide, not only is the potassium cyanide decomposed, but also the zinc cyanide; thus—

$$2KCy,ZnCy_2 + 4HCl = 2KCl + ZnCl_2 + 4HCy$$

Some of these double cyanides are decomposed by sulphuretted hydrogen, with precipitation of the sulphide of the heavy metal, *e.g.* $2KCy,HgCy_2$, $2KCy,CdCy_2$, and $2KCy,ZnCy_2$. In other cases, however, sulphuretted hydrogen fails to precipitate the metals as sulphides, *e.g.* $2KCy,CuCy_2$ or $6KCy,Cu_2Cy_2$, and $2KCy,NiCy_2$ (see also pp. 60 and 83).

All the double cyanides of this class are decomposed by being boiled with mercuric oxide, with the formation of mercuric cyanide and precipitation of the oxide or hydroxide of the heavy metal—

$$2KCy,NiCy_2 + 2HgO + 2H_2O = 2HgCy_2 + 2KHO + Ni(HO)_2$$

The detection of the cyanogen in these double compounds may

be accomplished by the same reactions as those already described for single cyanides. To recognise the heavy metal (as in the case of single cyanides), the compound must be *completely* decomposed by one of the various methods given, either by boiling with dilute hydrochloric acid, or by strong sulphuric acid, or by precipitation with mercuric oxide, or, where available, by means of sulphuretted hydrogen.

(2) **Difficultly decomposed Double Cyanides.**—These compounds are not decomposed with liberation of hydrocyanic acid by dilute mineral acids. They may be regarded as containing a complex metallo-cyanogen radical, represented by the general formula RCy_6; and in the case of those which are of most importance in analysis, R stands for Fe or Co, as in the following :—

Potassium ferrocyanide,	$K_4(FeCy_6)$
Copper ferrocyanide,	$Cu_2(FeCy_6)$
Potassium ferrous ferrocyanide,	$K_2Fe(FeCy_6)$
Ferric ferrocyanide (*Prussian blue*),	$Fe_4(FeCy_6)_3$
Potassium ferricyanide,	$K_3(FeCy_6)$
Ferrous ferricyanide (*Turnbull's blue*),	$Fe_3(FeCy_6)_2$
Potassium cobalticyanide,	$K_3(CoCy_6)$

The reactions which potassium ferro and ferri cyanides give with ferric and ferrous salts have already been studied in connection with the special tests for iron. The two salts of iron are therefore used for the detection of soluble ferro and ferri cyanides.

(*a*) **Ferrocyanides.**—The alkali ferrocyanides alone are easily soluble in water. By double decomposition, therefore, with potassium ferrocyanide and a metallic salt, the insoluble ferrocyanides are precipitated ; *e.g.*—

$$K_4(FeCy_6) + 2CuCl_2 = 4KCl + Cu_2(FeCy_6)$$

When treated with cold dilute acids, the ferrocyanides are decomposed, *not* with evolution of hydrocyanic acid, but with the formation of hydroferrocyanic acid, the complex cyanogen group remaining intact—

$$K_4(FeCy_6) + 4HCl = 4KCl + H_4(FeCy_6)$$

When boiled with dilute sulphuric acid, the alkali ferro (and "ferri") cyanides are *partially* decomposed, with elimination of a portion of the cyanogen as hydrocyanic acid. (This is the usual method for preparing aqueous hydrocyanic acid)—

$$2K_4(FeCy_6) + 3H_2SO_4 = K_2SO_4 + K_2Fe(FeCy_6) + 6HCy$$

When heated with strong sulphuric acid (in common with all cyanides) the cyanogen radical is completely decomposed, the nitrogen it contains being converted into ammonia—

$$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Insoluble ferrocyanides are decomposed by treatment with caustic alkalies and alkali carbonates; thus, with Prussian blue (ferric ferrocyanide)—

$$Fe_4(FeCy_6)_3 + 12NaHO = 2Fe_2(HO)_6 + 3Na_4(FeCy_6)$$

By removing the precipitated metallic hydroxide (in this case ferric hydroxide) by filtration, the presence of the ferrocyanide in the solution can be detected by the addition of ferric chloride.

Under the influence of oxidising agents (*e.g.* chlorine or bromine water) potassium ferrocyanide is converted into ferricyanide—

$$K_4(FeCy_6) + Cl = KCl + K_3(FeCy_6)\,*$$

(*b*) **Ferricyanides.**—The alkali salts only are easily soluble in water. Acids and alkalies act upon the ferricyanides as upon ferrocyanides; *e.g.* the insoluble compounds, when boiled with alkaline hydroxides, yield the soluble alkali ferricyanide, precipitating the metal as hydroxide; thus, with ferrous ferricyanide (Turnbull's blue)—

$$Fe_3(FeCy_6)_2 + 6NaHO = 2Na_3(FeCy_6) + 3Fe(HO)_2$$

Soluble ferricyanides are recognised by the formation of a blue precipitate with ferrous sulphate (see Iron). Insoluble ferricyanides (in common with all other double cyanides) are examined for the metals they contain by first decomposing the compound; either by boiling with alkali hydroxide as shown above, or by boiling with strong sulphuric acid; or, lastly, by fusion with a mixture of ammonium nitrate and sulphate, whereby the metals are converted into sulphates.

Cyanic Acid and Cyanates.

Cyanic Acid, HCyO.—This compound cannot exist in contact with water, being broken up into carbon dioxide and ammonia;

* Although for many reasons it is convenient to regard these compounds as containing the complex radical ($FeCy_6$), this view of their constitution somewhat obscures some of their reactions. The oxidation of potassium ferrocyanide to ferricyanide is a case in point. If these two compounds be represented as double compounds of "ferrous" and "ferric" cyanides respectively, then the oxidising action of chlorine in converting the one into the other is at once apparent—

$$4KCy,Fe''Cy_2 + Cl = KCl + 3KCy,Fe'''Cy_3$$

therefore, when cyanates are acted upon by acids, while the vapour of cyanic acid escapes, and is recognised by its powerful and pungent or acrid smell, the greater part of it is decomposed by the water present; thus—

$$2K(CN)O + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2\,SO_4 + 2CO_2$$

Cyanates of the alkalies and alkaline earths are soluble in water. Insoluble cyanates are therefore precipitated when salts of most of the heavy metals are added to a solution of potassium cyanate.

Ammonium cyanate, NH_4CNO, is isomeric with urea, $(NH_2)_2CO$, and when an aqueous solution of the former is heated, it passes into the latter, by simple rearrangement of the atoms already in the molecule without any addition or subtraction.

Cyanates are at once distinguished from cyanides, by the fact that they do not evolve hydrocyanic acid on treatment with dilute acids. They are identified by the evolution of carbon dioxide, with simultaneous formation of ammonium salt.

Commercial potassium cyanide usually contains potassium cyanate, which is detected by this reaction.

Thiocyanic Acid and Thiocyanates.

Thiocyanates are the sulphur analogues of the cyanates. The acid itself, HCyS (like cyanic acid), is unstable in aqueous solution. The chief insoluble thiocyanates are those of silver, lead, mercury, and copper. On the addition of solutions of these metals to a solution of potassium thiocyanate, the various compounds are precipitated. Silver thiocyanate, AgCyS, is obtained as a white precipitate resembling the chloride in appearance. It dissolves in ammonia, but less easily than either the cyanide or chloride, and is insoluble in dilute nitric acid.

With ferric salts, potassium or ammonium thiocyanates give a red colour, which is not destroyed by hydrochloric acid. The formation of this colour is employed both as a test for "ferric" iron or for thiocyanates. The addition of mercuric chloride destroys the colour.

When heated, the thiocyanates are decomposed. The potassium salt may be heated to fusion in the absence of air, but in contact with air it is converted into sulphate and cyanate, with evolution of sulphur dioxide. The mercurous and mercuric salts, when heated in contact with the air, take fire and burn, at the same time swelling up in a most remarkable manner,* leaving a straw-coloured voluminous ash, which is many times as bulky as the original compound. At the same time sulphur dioxide, mercury vapour, nitrogen, and cyanogen are evolved.

* The thiocyanates of mercury are the materials of which the so-called "Pharaoh's serpents" are made.

Silicon.

The properties of the element silicon, in the uncombined state, are not made use of in analysis, as in no analytical reactions is this element liberated.

Silicic Acid and Silicates.

Silicic acid, H_2SiO_3, is obtained, when soluble silicates are decomposed by acids, as a white gelatinous substance, slightly soluble in water, and still a little more soluble in acids—

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl$$

If the decomposition of the soluble silicate be made to take place in the presence of an excess of acid—that is, if the silicate be added to the acid (instead of adding acid to the silicate)—the silicic acid which is produced is not precipitated at once, but remains in solution, and may be separated from the sodium chloride and the excess of hydrochloric acid by dialysis. After a short time, however, the silicic acid separates out as a transparent gelatinous mass.*

Silicic acid is also precipitated from a solution of an alkali silicate by the addition of ammonium carbonate (ammonia does not cause any precipitate). The action may be regarded as taking place in two stages, ammonium silicate being first formed by double decomposition, and immediately breaking up into silicic acid and ammonia; thus—

$$Na_2SiO_3 + (NH_4)_2CO_3 = Na_2CO_3 + (NH_4)_2SiO_3$$
$$(NH_4)_2SiO_3 = 2NH_3 + H_2SiO_3$$

Silicic acid is a very feeble acid, and when heated to 130° C. it parts with a molecule of water and is converted into silicon dioxide (*silica*), SiO_2, a compound which is insoluble in water and in acids.†

Silica, SiO_2, occurs in a more or less pure state in nature, in the form of *quartz*, *flint*, *agate*, *sand*, etc. When prepared artificially by heating the hydrated compound, it is a white amorphous powder. It is extremely stable, and capable of standing a very high temperature. It is insoluble in water and all acids except hydrofluoric acid. It dissolves in caustic alkalies; and, when in the amorphous

* The acid which is thus obtained in solution is believed to be the less stable tetrabasic silicic acid, H_4SiO_4, or $Si(HO)_4$, or $SiO_2,2H_2O$. This compound, by giving up one molecule of water, passes into the dibasic acid, H_2SiO_3, or SiO_2,H_2O.

† Silicic acid is sometimes spoken of as *soluble silica*, and silicon dioxide as *insoluble silica*.

state, in boiling carbonates of the alkalies, yielding in all cases the soluble alkali silicates.

The only silicates which are soluble in water are the alkali silicates (known as *water glass*, or *soluble glass*). The natural silicates form a numerous and complex class of minerals. They may be regarded as compounds of metallic oxides with silicon dioxide; thus, *felspar*, $Al_2O_3,K_2O,6SiO_2$.

The silicates, which are insoluble in water, may be classified for analytical purposes into (1) those which are decomposed by acids (other than hydrofluoric acid); and (2) those which are unattacked, which comprises by far the larger class.

The presence of silica in these compounds is detected by means of their behaviour when heated with microcosmic salt. A clear bead of this salt is made upon a loop of platinum wire, and a few small particles of the powdered mineral are heated in it. The metallic oxides are dissolved by the fused microcosmic salt, but not the silicon dioxide, particles of which (the skeletonic remains of the mineral) remain floating about in the molten bead.*

Silica may also be detected by the formation of silicon fluoride, when a silicate is acted upon by hydrofluoric acid. The test is made as described under fluorine (p. 134).† In this case, however, the drop of water which is suspended in the gas in order to detect the silicon fluoride, should be held on a loop of platinum wire, as the action of the hydrofluoric acid upon the glass rod might be mistaken for a deposition of silica. When applying this test for the detection of fluorine, this is obviously no disadvantage.

(1) **Silicates which are decomposed by acid** may have their silica removed by treatment with hydrochloric acid, just as in the case of the alkali silicates above mentioned. In this instance, however, the mineral, in as finely powdered a condition as possible, is digested with strong hydrochloric acid at a gentle heat, when gelatinous silicic acid separates, and the powdered mineral gradually dissolves. In order to render the separation of the silica complete, the mixture is next evaporated to dryness (preferably on a steam-bath), and in order to ensure the entire conversion of the silicic acid into silica, it is afterwards gently heated over a flame for a short time: (excessive heating is to be avoided, as certain metallic oxides are thereby rendered very difficult of subsequent solution in acid). The residue is then treated with a small quantity of strong hydrochloric

* This preliminary test, however, is not absolutely reliable. Some insoluble silicates are known which do not leave this residue, and there are certain natural phosphates which are not dissolved by fused microcosmic salt, but remain floating in the bead, and might be mistaken for silica.

† Except that a platinum crucible must replace the test-tube.

acid ; water is added, and the solution containing the metals present as chlorides is separated by filtration from the insoluble residue of silica.

(2) **Silicates which are unattacked by acids** are decomposed by fusion with alkali carbonates. The finely powdered silicate is mixed with several times its weight of *fusion mixture*, and the mixture heated in a platinum crucible. As the mass melts, effervescence takes place, due to the escape of carbon dioxide ; thus, using a general formula for a simple silicate *—

$$x\mathrm{RO}.y\mathrm{SiO_2} + y\mathrm{Na_2CO_3} = x\mathrm{RO} + y\mathrm{Na_2SiO_3} + y\mathrm{CO_2}$$

The fusion is continued until effervescence ceases, the temperature being raised towards the end of the operation. The residue, after cooling, is extracted with water, which dissolves the alkali silicate (and excess of carbonate), leaving the metallic oxide (or carbonate). Hydrochloric acid is then gradually added, which causes the precipitation of silicic acid, and at the same time dissolves the metallic oxides. The mixture is then evaporated, and treated in the manner described above.

The acid radicals of any other compounds present in the silicate (*e.g.* sulphates, phosphates, borates, arsenates, chlorides) are now present as their sodium or potassium salts, and may be detected by their several special tests in the ordinary way.

This method of fusion with alkali carbonates is obviously inadmissible in the case of natural silicates which are suspected of containing the alkali metals, and which are insoluble in hydrochloric acid. In this case, one of the following plans may be employed:—

(*a*) **Heating with Barium Oxide.**—A small quantity of the finely powdered mineral is intimately mixed with three or four times its weight of barium oxide, and strongly heated in a platinum crucible by the blowpipe, the heating being continued for about twenty minutes. The mass is then dissolved in dilute hydrochloric acid. The solution so obtained is made alkaline with ammonia (a precipitate is produced, which need not be removed), and ammonium carbonate is added. The mixture is then filtered, and the filtrate evaporated to dryness and heated, and examined for the alkalies in the usual way (p. 25).

(*b*) **Heating with Ammonium Chloride and Calcium Carbonate.**—A small quantity of the powdered silicate is mixed with about an equal weight of ammonium chloride and about eight

* The possibility of this reaction depends upon the fact that, although silicic acid is an unstable acid, silicon dioxide and the alkaline silicates are extremely stable even at high temperatures.

times its weight of calcium carbonate (precipitated), and the mixture gently heated in a platinum crucible until no more fumes of ammonium chloride are given off. It is then strongly heated with the blowpipe for about fifteen minutes, after which the mass is treated with water. The alkalies, in the form of chlorides, together with a small quantity of calcium chloride, pass into solution, and are separated by filtration. The calcium is removed by precipitation with ammonium carbonate, and the filtrate evaporated and examined for alkalies.

(*c*) **Decomposing the Silicate with Hydrofluoric Acid.**—This may be accomplished by treating the powdered mineral with aqueous hydrofluoric acid in a platinum crucible, gently evaporating the liquid (in a draught cupboard) to dryness, adding fresh acid and evaporating again, continuing the operation until the residue is entirely soluble in hydrochloric acid. Or the mineral may be moistened with a little strong ammonia in a platinum crucible, and the whole exposed to the action of gaseous hydrofluoric acid (generated from fluorspar and sulphuric acid) in a leaden pot, which can be covered with a leaden lid. The action is allowed to proceed for at least twenty-four hours. The crucible is then removed, and the ammonium fluoride expelled by gently heating in a draught cupboard.

Boron.

The properties of the free element are not employed in analysis.

Boric Acid and Borates.

Boric acid, H_3BO_3, is a white crystalline solid, sparingly soluble in cold, but more readily soluble in hot, water. It is deposited from its solutions in the form of pearly white scales.

It is also soluble in alcohol, and when either the aqueous or alcoholic solution is boiled, the acid vaporises along with the solvent.

When heated, boric acid (ortho), H_3BO_3, loses water, passing first into metaboric acid, $H_2B_2O_4$, and finally into pyroboric acid, $H_2B_4O_7$.

The borates of the alkalies are readily soluble in water; most other borates are insoluble. A few (*e.g.* magnesium borate) are difficultly soluble. The most familiar salts are those of pyroboric acid, *e.g.* ordinary borax, $Na_2B_4O_7$.

The insoluble borates obtained by precipitation are not characteristic, and are not used in analysis for the detection of borates.

All borates are decomposed by mineral acids, with liberation of orthoboric acid ; thus—

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

Reaction with Turmeric.—Boric acid produces upon turmeric paper a characteristic red-brown stain. This coloration is distinguished from that produced by alkalies (which it closely resembles in appearance) by the fact that when touched with an alkali the brown colour is changed to a greenish-black, but is restored to its original tint by dilute acids (HCl or H_2SO_4). The borate is moistened with hydrochloric or sulphuric acid in order to liberate the boric acid, and a drop or two of the liquid is poured upon the turmeric paper.

Flame Reactions.—Volatile boron compounds impart a characteristic green colour to a non-luminous flame; thus, when an alcoholic solution of boric acid is boiled, and the alcohol vapour inflamed, the green colour due to the volatilised boric acid is apparent. The test is made in the following manner :—

The borate (borax) is moistened with a little strong sulphuric acid in a test-tube or small flask, and alcohol is added. The test-tube is closed with a cork carrying a short straight glass tube. The contents of the tube are then heated, and as the alcohol boils off it is inflamed at the exit tube, when the green colour of the flame is observed.

Since ethyl chloride (which is liable to be formed if a metallic chloride is treated in the same manner) gives a flame which also has a green edge or fringe (albeit, if this compound were formed, the alcohol flame would at once be rendered luminous, like an ordinary gas flame), the following test may also be applied as a confirmation :—

A small quantity of the powdered borate (or boric acid) is mixed with about its own weight of powdered calcium fluoride and three or four times its weight of hydrogen potassium sulphate. This mixture is moistened with the least drop of water, and a little of the paste is introduced into a Bunsen flame upon a loop of platinum wire. By the action of the acid sulphate upon the fluoride, hydrofluoric acid is formed; and this in the presence of the borate gives boron fluoride, BF_3, which causes a green coloration of the flame :—

$$(1)\quad CaF_2 + 2HKSO_4 = CaSO_4 + K_2SO_4 + 2HF$$
$$(2)\quad B_2O_3 + 6HF = 3H_2O + 2BF_3$$

In many cases it is sufficient to mix the borate with the fluoride, and moisten the mixture with a drop of strong sulphuric acid and bring this into the flame in the same way. The presence of copper salts masks the reaction.

CHAPTER XV.

Systematic Detection of the Acids.

The acids are classified into three main groups based upon the solubility of their barium and silver salts.

Group I.—Acids whose barium salts are precipitated from *neutral* solutions by barium chloride.

(*a*) Whose barium salts are insoluble in dilute hydrochloric acid—

Sulphuric acid,	H_2SO_4	Hydrofluosilic acid,	H_2SiF_6*

(*b*) Whose barium salts are soluble in hydrochloric acid—

Carbonic acid,	H_2CO_3	Boric acid,	H_3BO_3
Sulphurous ,,	H_2SO_3	Iodic ,,	HIO_3
Thiosulphuric acid,	$H_2S_2O_3$	Hydrofluoric acid,	HF
Silicic ,,	H_2SiO_3	Oxalic ,,	$H_2(C_2O_4)$†
Chromic ,,	H_2CrO_4	Tartaric ,,	$H_2(C_4H_4O_6)$†
Phosphoric ,,	H_3PO_4	Citric ,,	$H_3(C_6H_5O_7)$†

Group II.—Acids whose silver salts are precipitated by silver nitrate from solutions acidified with nitric acid—

Hydrochloric acid,	HCl	Sulphuretted hydrogen,	H_2S
Hydrobromic ,,	HBr	Thiocyanic acid,	HCyS
Hydriodic ,,	HI	Ferrocyanic ,,	H_4FeCy_6
Hydrocyanic ,,	HCy	Ferricyanic ,,	H_3FeCy_6

Group III.—Acids whose barium salts are soluble in water, and whose silver salts are not precipitated in a nitric acid solution, namely—

Nitric acid,	HNO_3		
Nitrous ,,	HNO_2	Cyanic acid,	HCyO

* Soluble in strong hydrochloric acid.

† In the case of these three acids, the neutral solution must not contain appreciable quantities of ammoniacal salts, or soluble double compounds are formed on addition of barium chloride, which may entirely prevent the formation of a precipitate.

Chloric acid,	$HClO_3$	Formic acid,	$H(CHO_2)$
Perchloric acid,	$HClO_4$	Acetic „	$H(C_2H_3O_2)$

As already mentioned (p. 120), these general reagents, barium chloride and silver nitrate, are not employed to effect the *separation* of groups of acids, but rather as indicators of the presence or absence of entire groups.

In most cases, each acid is individually tested for in separate portions of specially prepared solutions (see below).

The examination for acids should be made *after* the metals have been detected, for two reasons: firstly, because during the course of the systematic examination for the metals, the presence or absence of quite a number of acids will be incidentally ascertained; and secondly, because a knowledge of what metals are present will be a guide to the student in deciding what acids *may* and what *cannot possibly* be present. For example, if the material under examination is a *solution* having an *acid* reaction, and it is found to contain *silver* as one of the metals, it will obviously be useless to expect to find any of the acids of Group II. Or if the substance is a solid which dissolves easily in water, and *calcium* is found, it is equally unnecessary to apply tests for sulphuric, phosphoric, carbonic, silicic, hydrofluoric or other acids whose calcium salts are not easily soluble in water. Or if a solid, soluble in water, were found to contain the metal lead, the acids most probably present would be nitric or acetic, as the lead salts of these two acids are the only common soluble lead compounds. A student who, in spite of this, goes blindly through a series of tests for acids which cannot be present, shows at once that he has no intelligent appreciation of the work he is doing.

It will be evident that, in order to make the fullest use of the information he has gained concerning the metals that are present, the student must have a knowledge of the solubilities of a large number of compounds. The solubility of the common compounds of the metals and acids has been mentioned under the separate elements treated in the foregoing chapters; but in order to make the information more accessible for reference, a condensed epitome of solubilities of the common compounds of the various metals and acids which have been treated, is given at the end of this chapter (p. 177).

As stated above, several acids will be detected during the examination for metals; thus—*on acidifying with hydrochloric acid* and gently warming (for separation of Group I.), the presence of *carbonates*, *sulphites*, *sulphides*, *cyanides*, or *nitrites* will be

indicated by the evolution of carbon dioxide, sulphur dioxide, sulphuretted hydrogen, hydrocyanic acid, or nitric oxide (appearing as brown fumes of the peroxide) respectively.*

The evolution of sulphur dioxide with simultaneous deposition of sulphur indicates *thiosulphates*. The escape of chlorine may denote *hypochlorites*, or may arise from the action of the hydrochloric acid (especially if not very dilute) upon *chlorates*, *iodates*, *chromates*, *nitrates*, or (in the case of solid substances) of *peroxides*.

When the substance under examination is a solid, these indications obtained by the action of hydrochloric acid should be followed up by a second general test, namely—

Treatment with Strong Sulphuric Acid.—On gently warming a little of the solid with a small quantity of concentrated sulphuric acid in a test-tube, a number of important indications may be obtained; thus, *Cyanides*, *chlorides*, *fluorides*, and *nitrates* evolve their respective acids, in the latter case accompanied by brown fumes. *Iodides* give violet vapours; *bromides* give the dark-brown vapour of bromine, condensing to dark drops on the tube; *chlorates* yield the deep yellow explosive gas, chlorine peroxide. *Formates* evolve carbon monoxide, while *oxalates* give carbon monoxide and dioxide (the residue in neither case is blackened). *Tartrates* and *citrates* evolve sulphur dioxide in addition to the oxides of carbon, at the same time leaving a black residue. In many cases these indications should be followed up at once by special confirmatory tests, which it may be practicable to apply directly to the substance under investigation; *e.g.* an indication which leads to the suspicion of nitrates being present, should be confirmed by applying the test with copper, or the ferrous sulphate reaction. If, therefore, this test with sulphuric acid should give a purely negative result, it is obvious that a large number of acids are excluded. The chief compounds which give no indications when subjected to this test are sulphates, phosphates, phosphites, arsenates, silicates, and metallic oxides other than peroxides, or such as behave as peroxides; these latter evolve oxygen.

On treatment with sulphuretted hydrogen, in the separation of the metals of Group II., indications will have been obtained of the presence of *chromates* and *iodates*: the former by the change of colour from orange to green, with simultaneous precipitation of sulphur; the latter by the elimination of iodine, which

* If these indications of the decomposition of salts of these acids were not carefully noted during the examination for metals, the reaction should be repeated at this stage of the analysis.

gives a dark brown colour to the solution, the colour gradually disappearing as the excess of sulphuretted hydrogen converts the iodine into hydriodic acid.

On the preparation of the solution for separating the metals of Group III., the presence or absence of *phosphates* and *silicates* will have been ascertained, and also of such organic acids (citric or tartaric) as leave a charred residue when heated.

Besides these, indications of the presence of several acids will have been obtained during the performance of the general dry tests for the metals (p. 179).

Preparation of the Solution for the Detection of Acids.

Before testing for the acids, it is advisable (in many cases it is *necessary*) that they should be present in the solution as salts of the alkalies (or alkaline earths); that is to say, the metals with which the various acids are united in the substance under analysis should be exchanged, by double decomposition, for an alkali metal; for the reason that the presence of these other metals would in many cases mask the reactions by which the acids are to be detected.* To accomplish this, the solution is boiled,† and sodium carbonate added in quantity slightly in excess of that required to effect complete precipitation. The mixture is then filtered, and the acids, now present as their sodium salts, are detected in the solution.‡

* Whether or not this would be the case will usually be revealed by the result of the examination for metals. For example, suppose the metals found in a solution were magnesium and copper, then the only acids likely to be present would be hydrochloric, sulphuric, and nitric (these acids forming the common soluble salts of the two metals), and the reactions by which these acids may be detected can be made equally well whatever metal they may be united with. Or again, suppose, in addition to these two metals, silver was found; this would reduce the acids probably present to nitric and sulphuric, and the test for the latter would then merely require the substitution of barium nitrate for barium chloride. The student should therefore use an intelligent judgment at this point, and not proceed by a blind habit to prepare the solution by the removal of the metals with sodium carbonate, whether such a step be necessary or not. The importance of carefully and systematically taking notes of his work *as it is in progress* cannot be too strongly urged. Such notes should be recorded as *important memoranda for his own guidance and instruction*, and not as a mere voucher for his teacher that he has carried out a certain prescribed process, or made a certain stereotyped set of tests.

† In cases where the substance under analysis is insoluble, the product obtained by fusion with sodium carbonate is extracted with water, and the solution so obtained is employed for the detection of the acids (see p. 184).

‡ This method for separating the metals from their acids is not, however, of universal application. Thus, in the case of many of the phosphates held in solution by acids, the action of the sodium carbonate is to cause the precipitation of the *phosphates themselves;* in such instances, therefore, the acid is not found in the solution. Since, however, phosphoric acid will have been

GENERAL TESTS.—(1) A small portion of this solution is carefully neutralised by first adding dilute nitric acid drop by drop (the mixture being heated to expel carbon dioxide), until the liquid is *just acid*, and then adding a drop or two of dilute ammonia.

This neutral solution is then tested by the addition of barium chloride. If no precipitate is obtained, the acids of Group I. (p. 171) are absent. If a precipitate is formed which redissolves on the addition of hydrochloric acid, the two acids sulphuric and hydrofluosilicic are excluded.

(2) A second small portion of the solution is acidified with nitric acid, and tested with silver nitrate. A negative result proves the absence of the acids of Group II.

If these general tests show that acids of both Groups I. and II. are present, special tests must then be applied in separate portions of the solution, for such acids as, from information already gained, are considered likely to be in the substance under analysis, and which have not been definitely discovered during the course of the examination. The tests may be made in accordance with the following outline scheme, in which most of those acids which must certainly have been detected in the earlier stages are not again mentioned.

A. *In portions of the solution acidulated with hydrochloric acid.*

Sulphuric Acid.—Barium chloride precipitates white barium sulphate : not dissolved by the addition of strong hydrochloric acid, and boiling the liquid.

Hydrofluosilic Acid.—Barium chloride gives white barium silicofluoride : soluble in strong hydrochloric acid.

Ammonia precipitates gelatinous silicic acid.

Silicic Acid.—Ammonium carbonate (but not ammonia) precipitates silicic acid.

"Ferro" and **"ferri"-cyanic acids** * give their respective reactions with iron salts.

Thiocyanic acid * gives the red coloration with ferric salts.

discovered during the examination for the metals, this fact is of little consequence.

On the other hand, sodium carbonate fails to separate the metals from cyanides soluble in water (mercuric cyanide) or in potassium cyanide (*i.e.* soluble double cyanides, such as those of silver, copper, zinc, etc.), and also from double tartrates and citrates, etc. In such cases as these, the metals may be separated by means of sulphuretted hydrogen or ammonium sulphide (see Reactions for cyanides, p. 161).

It will be obvious that *carbonates* must be detected at an earlier stage in the analysis.

* If the general test, No. 2 (see above), gave a negative result, these acids will have been proved to be absent.

Arsenic Acid.—If arsenic has been found among the metals and its state of oxidation (*i.e.* whether present as an arsenite or arsenate) has not been determined, the following test may be applied: Ammonium chloride, ammonia, and magnesium sulphate are added—a white precipitate may be due to either a phosphate or arsenate. If phosphoric acid has been proved to be absent (by the molybdate reaction), it must be the arsenate. In either case it should be filtered, and after being washed free from ammonium chloride, it is dissolved in a little nitric acid, and silver nitrate added (or a drop or two of silver nitrate may be poured upon the washed precipitate in the funnel). A brown precipitate indicates an arsenate.

B. *In portions acidulated with nitric acid.*

Hydrochloric, Hydrocyanic, and Thiocyanic Acids.—Silver nitrate gives a white precipitate.

Hydrobromic and Hydriodic Acids.—Silver nitrate gives a yellowish precipitate.

(For the methods of discriminating between these, see pp. 127 and 128.)

C. *In portions acidulated with acetic acid.*

Oxalic Acid.—Calcium sulphate precipitates calcium oxalate: readily soluble in hydrochloric acid.

Hydrofluoric Acid.—Calcium sulphate or chloride precipitates calcium fluoride: only slightly soluble in hydrochloric acid.

(Chromic, phosphoric, and arsenic acids may also be looked for in portions of this solution. These acids, however, will have been detected at an earlier stage of the analysis.)

D. *In portions rendered neutral.*

Tartaric and Citric Acids.—Calcium chloride gives a white precipitate of calcium tartrate in the cold, and of calcium citrate on boiling (see Special reactions, p. 157).

Formic and Acetic Acids.—Ferric chloride produces a red-coloured solution, browner in colour than that given by thiocyanates. The colour is destroyed by hydrochloric acid (see Special reactions).

TABLE OF SOLUBILITY.

1 = Soluble in water. 2 = Sparingly soluble in water, readily soluble in acids. 3 = Insoluble in water, soluble in acids.
4 = Insoluble in water, sparingly soluble in acids. 5 = Insoluble in water, insoluble in acids.

	O	S	Cl	Br	I	F	$(CN)^{i}$	$(ClO)^{i}$	$(ClO_3)^{i}$	$ClO_4)^{i}$	$SO_4{}^{ii}$	$(SO_3)^{ii}$	$(S_2O_3)^{ii}$	$(NO_3)^{i}$	$(NO_2)^{i}$	$(PO_4)^{iii}$	$(CO_3{}^{ii}$	$(C_2O_4)^{ii}$	$(SiO_3)^{ii}$	$(BO_3)^{iii}$	$(CrO_4)^{ii}$	$(AsO_3)^{iii}$	$(AsO_4)^{iii}$
Na ...	1	1	1	1	1	1	1	All hypochlorites are soluble in water.	All chlorates are soluble in water.	All perchlorates are soluble in water.	1	1	1	All nitrates are soluble in water.	All nitrites are soluble in water.	1	1	1	1	1	1	1	1
K.....	1	1	1	1	1	1	1				1	1	1			1	1	1	1	1	1	1	1
(NH_4)	—	1	1	1	1	1	1				1	1	1			1	1	1	—	1	1	1	1
Mg ...	3	1	1	1	1	4	1				1	1	1					2			1		
Ba ...	1	1	1	1	1	4	2				5		2					3			3		
Sr ...	2	1	1	1	1	4	1				4							3			2		
Ca ...	2	1	1	1	1	4	1				4							3			2		
Zn ...	3	3	1	1	1	2	3				1							3			1		
Mn ...	3	3	1	1	1	3	3				1							3			1		
Ni ..	3	3*	1	1	1	2	4				1							3			3		
Co ..	3	3*	1	1	1	2	4				1							3			3		
Fe^{ii} ..	3	3	1	1	1	2	4				1							3			—		
Fe^{iii} ..	3	3	1	1	1	1	—				1							3			—		
Cr.....	3	—	1†	1†	1	1	3				1							2			—		
Al.....	3	—	1	1	1	1	—				1							3			—		
Bi...	3	3	1‡	2	3	1	—				1							3			3		
Cu ..	3	3	1	1	4	3	4				1							3			1		
Cd ..	3	3	1	1	1	2	3				1							3			1		
Sb ..	3	3	1‡	1‡	2	1	—				1‡							3			—		
Sn^{ii} ..	3	3	1	—	1	1	—				2							3			2		
Sn^{iv} ..	4	3	1	—	1	1	—				2							3			3		
Au ..	—	3*	1	1	3	—	1				2							3			3		
Pt.....	—	3*	1	1	5	—	1				4							3			4		
Hg^{ii}...	3	3*	1	1	3	2	1																
$(Hg_2)^{ii}$	3	—	4	4	3	—	—																
Ag ..	3	3	5	5	5	1	5																
Pb ..	3	3	2	2	2	3	3																

* Soluble only in *aqua regia*. † Anhydrous compounds, solubility 5.
‡ Converted by the action of water into basic compounds, solubility 3.

CHAPTER XVI.

PRELIMINARY TESTS AND OPERATIONS IN A SYSTEMATIC ANALYSIS.

A. **When the Substance under Examination is a Liquid.**—Before proceeding to the separation of the groups, the liquid should be carefully tested with litmus paper, in order to ascertain whether it is neutral, acid, or alkaline.

(1) *If neutral*, the liquid might be simply water. To ascertain whether or not it contains anything in solution, a little of it should be carefully evaporated to dryness. This should be done upon a watch-glass, which is heated upon a steam-bath. (The glass may be placed over the mouth of a small beaker, in which a little water is being gently boiled.) If there is no residue left in the watch-glass when the liquid has entirely evaporated, it contained no salts in solution, and was therefore simply water.

[Unless evaporated gently as described, certain compounds which could be present might volatilise entirely, and in this way be altogether overlooked; *e.g.* ammonium nitrate would go off as steam and nitrous oxide, if its aqueous solution were merely boiled to dryness.]

(2) *If acid*, the solution may contain either a free acid, or salts possessing an acid reaction. [Either certain normal salts, *e.g.* copper sulphate, alum, etc., or certain "acid" salts, as hydrogen sodium sulphate. It must be remembered that many of the so-called "acid" salts, that is, salts in which the whole of the replaceable hydrogen has not been exchanged for metal, are not *acid* in the sense of exhibiting an acid reaction towards litmus; some are neutral, while others are alkaline; *e.g.* hydrogen sodium carbonate, hydrogen disodium phosphate, etc.].

(3) *If alkaline*, the liquid may contain either free alkali, or salts having an alkaline reaction.

B. **When the substance under analysis is a solid,** it should be critically examined, in order, if possible, to gain any

information from its general physical properties which may help to identify it. If crystalline, the colour, shape, etc., of the crystals should be noted. If powdered, it may be examined with a pocket-lens, in order to discover whether or not it is homogeneous ; *i.e.* whether it is a single compound, or a mixture of more than one.

The substance should then be subjected to the following general tests * :—

I. **The Flame Reaction.**—A small quantity of the substance is introduced into the edge of the Bunsen flame (first in the cooler region near the base of the flame, and afterwards in the hotter parts near the top of the interior cone) upon a loop of clean platinum wire. By a close observation of the *colour* imparted to the flame, compounds of *sodium*, *potassium*, *lithium*, *barium*, *strontium* *calcium*, *copper*, and *boron* may be indicated (see Reactions of these metals). *Borates* and certain *thio-cynates* (*e.g.* of mercury) behave in characteristic fashion when heated.

II. **The Borax Bead.**—By heating a minute particle of the substance in a borax bead in the blowpipe flame, both inner and outer flame, indications may be obtained of the presence of compounds of *cobalt*, *nickel*, *manganese*, *iron*, *chromium*, *copper*. [Should this test lead to the suspicion that either manganese or chromium is present, it should be followed up by the fusion of a portion of the substance with sodium carbonate and nitre upon platinum foil. See Manganese and chromium reactions.]

III. **The Blowpipe Reaction upon Charcoal.** (*a*) *When heated alone.*—A considerable amount of information may be obtained by heating a little of the substance by itself upon charcoal.

(1) *If it melts and is absorbed into the charcoal*, it points to the substance consisting of salts of the alkalies. [Chlorates and nitrates cause vivid combustion of the charcoal.]

(2) *If a white infusible residue is obtained*, the substance may consist of oxides (or salts which yield oxides when heated) of the *alkaline earth metals*, *alumina*, *zinc* (ZnO yellow while hot, white when cold), or of silica. [If the residue, when placed upon a piece

* Every smallest detail of these preliminary tests should be carefully and systematically noted down, whether the interpretation of the observed phenomena is obvious to the student or not. Indeed, it is often just those very points which at the time do not convey any definite information to him which may prove to be most important.

The examples which are here given of the changes that may take place when substances are submitted to the various general tests, must be regarded merely as *examples*. It would be obviously impossible to describe and tabulate every result which might be obtained by subjecting the infinite variety of possible mixtures to the tests described, and even if it were possible, it would be quite undesirable to do so.

of turmeric or litmus paper and moistened with water, shows an alkaline reaction, it will contain one of the alkaline earth metals. Silica may be specially tested for by the bead of microcosmic salt.]

(3) *If a coloured residue is left*, it points to one of the metals already indicated by the borax-bead test.

(4) *If reduction takes place*, resulting in the formation of fumes and an incrustation upon the charcoal, without indication of a metallic bead, it points to the presence of compounds of very volatile metals, as *arsenic* (white incrustation accompanied by garlic odour), *cadmium* (red-brown incrustation), *zinc* (incrustation yellow when hot, and forming very close to the substance). Such a volatile compound as *ammonium chloride* gives white fumes and an incrustation (the latter being formed at a considerable distance from the heated spot). In this case the blowpipe flame appears of a yellow-ochre colour as it impinges upon the ammonium salt.

(*b*) *When heated with Reducing Agents.*—When the substance is mixed with sodium carbonate and potassium cyanide, and heated upon charcoal in the reducing flame, compounds of *copper*, *silver*, and *gold* are reduced to the metallic state without giving any incrustation upon the charcoal; while compounds of *antimony*, *bismuth*, *tin*, and *lead* give metallic beads accompanied by incrustations (for the characteristics of the incrustations and the metals, see Special reactions of each).

IV. **The Action of Heat.**—The behaviour of a substance when heated alone in a dry narrow tube closed at one end (a small test-tube), will generally afford important information respecting its composition.

(*a*) IF THE SUBSTANCE SIMPLY MELTS, AND SOLIDIFIES AGAIN ON COOLING, without giving off any gases or vapours, a large number of compounds are obviously at once excluded. In this case the substance may consist of salts of the alkalies or the alkaline earth metals; a few white salts of the heavy metals, *e.g.* silver chloride; or a few coloured salts, *e.g.* lead chromate.

(*b*) IF WATER IS GIVEN OFF, collecting in drops upon the upper part of the tube, it may be due (1) to hygroscopic * moisture (in this case the amount will probably be small), (2) to the decomposition of metallic hydroxides, or (3) to water of crystallisation. [Substances containing much water of crystallisation, when heated, often melt *twice*—first in the water of crystallisation, and as this is

* That is moisture due to the substance being "damp"—mechanically adhering moisture. Almost all powders attract a little moisture in this way from the atmosphere.

expelled they resolidify, but on the application of a stronger heat they once more undergo fusion.]

The water should be carefully tested by introducing a small strip of litmus paper.

Alkalinity would indicate ammonium compounds (*e.g.* $(NH_4)_2MgPO_4$, $HNa(NH_4)PO_4$, etc.).

Acidity might be due to the decomposition of certain acid salts, either alone or by interaction with other salts (*e.g.* hydrogen potassium sulphate, when heated, is converted into the normal salt and sulphuric acid, and if present along with a salt containing water of crystallisation, the water would become acid ; or if mixed with sodium chloride or nitrate, hydrochloric acid or nitric acid would be evolved by double decomposition).

(*c*) IF THE SUBSTANCE CHANGES COLOUR—

(1) From white to yellow, indicates oxide of zinc, tin, bismuth ;

(2) From yellow to brown (fusing at a red heat), oxide of lead.

Most coloured oxides become much darker when heated (*e.g.* HgO, Fe_2O_3).

(*d*) IF GASES OR VAPOURS ARE EVOLVED, they must be identified by special tests.

(1) Oxygen and nitrous oxide (re-ignition of glowing splint of wood). The former from chlorates, iodates, bromates, nitrates, or peroxides ; the latter from ammonium nitrate, or salts which by double decomposition give ammonium nitrate.

(2) Hydrogen (character of flame), from formates, and from oxalates in presence of caustic alkalies or alkaline earths ($K_2C_2O_4 + 2KHO = 2K_2CO_3 + H_2$).

(3) Nitrogen (extinguishes flame, and gives no reaction with lime-water), from ammonium nitrite or chromate, or from mixtures which yield these salts by double decomposition.

(4) Chlorine, bromine, and iodine (recognised by colour, smell, etc.), evolved from certain halogen compounds when heated alone, or in admixture with acid salts and peroxides (*e.g.* a mixture containing such compounds as NaCl, $HKSO_4$, and MnO_2, when heated, evolves chlorine).

(5) Sulphur vapour (sublimate of yellow drops), from metallic persulphides.

(6) Carbon dioxide (action on lime-water), from most carbonates other than the normal salts of the alkalies (also, mixed with carbon monoxide, from certain formates and oxalates).

(7) Sulphur dioxide (characteristic odour), from certain sulphites (*e.g.* $CaSO_3 = CaO + SO_2$), certain sulphates (*e.g.* $2FeSO_4$

$= Fe_2O_3 + SO_3 + SO_2$; $CuSO_4 = CuO + SO_2 + O$). It may also be due to the oxidation of sulphur evolved from sulphides or other sulphur compounds, as thiocyanates.

(8) Cyanogen (formation of thiocyanate of ammonia), from certain metallic cyanides.

(9) Ammonia (odour, and action on test-paper), from many ammonium salts; *e.g.* sulphate, phosphate, carbonate, etc. (also from the decomposition of cyanates).

(10) Sulphuretted hydrogen (odour, and action on paper moistened with lead acetate), from the decomposition of hydrated metallic sulphides, of sulphites and thiosulphates, in the presence of compounds which yield water or acid.

(11) Phosphoretted hydrogen (odour, and character of flame), from hypophosphites.

(12) Nitrogen peroxide and oxygen, from the decomposition of nitrates of heavy metals, or from mixtures which by double decomposition yield such a compound (*e.g.* $PbSO_4$ and KNO_3).

(*e*) IF A SUBLIMATE IS PRODUCED, it indicates such volatile solids as the following :—

(1) Giving a white sublimate—ammonium haloid salts, arsenious oxide, mercuric chloride, mercurous chloride (yellowish while hot, white on cooling).

(2) Giving a coloured sublimate—mercuric iodide (red and yellow), arsenious sulphide (yellow).

(3) Giving a black metallic-looking sublimate—iodine (violet vapours), mercuric sulphide (red streaks if rubbed with a glass rod), metallic mercury (runs into liquid globules when rubbed with a glass rod), metallic arsenic (garlic smell). [If this test leaves it doubtful whether arsenical or mercurial compounds are present, a little of the substance should be mixed with sodium carbonate and heated in a dry tube. If mercurial, the sublimate consists of minute globules.]

Ammoniacal compounds may be at once tested for by heating a portion of the substance with a little sodium hydroxide, when ammonia is evolved.

(*f*) IF NO CHANGE TAKES PLACE, it will be evident from the foregoing that the number of substances which can possibly be present is extremely limited; and if in addition the compound is *white*, the range of probable substances is still further narrowed down to the oxides of a few of the metals, such as the alkaline earths, alumina, silica, etc.

To obtain a Solution of the Solid Substance. (1) **In**

Water.—A small quantity of the substance, in a finely powdered condition, is first treated with cold water in a large test-tube. [This may result in the evolution of gas, owing to the chemical action of water upon such compounds as certain metallic phosphides (*e.g.* calcium phosphide) or carbides (calcium carbide), which evolve phosphoretted hydrogen and acetylene respectively; or carbon dioxide might be expelled, owing to the presence of soluble carbonates and acid salts, which would interact upon each other.] The mixture is then boiled for a few moments.

If the substance does not dissolve, it is either wholly or partly insoluble in water. To ascertain whether any of it has dissolved, the mixture should be allowed to settle, and a few drops of the clear liquid evaporated to dryness upon a watch-glass; or upon a piece of platinum foil, cautiously heated. If a residue is obtained on evaporation (thus showing that partial solution in water has taken place), the aqueous liquid is decanted off (or filtered if the insoluble part does not readily settle), and the insoluble portion again boiled with water and filtered.

(2) **In Acids.**—The portion insoluble in water is then treated with dilute hydrochloric acid and boiled. If it does not entirely dissolve, the dilute acid is decanted off into another test-tube, and strong hydrochloric acid substituted,* the mixture being submitted to prolonged boiling, if necessary. If the substance wholly dissolves, the two acid solutions may be mixed together.

If, on adding a few drops of the aqueous extract to a small portion of the acid solution, no precipitation takes place, the main portions of the two solutions may be mixed together † and examined for metals and acids (except hydrochloric acid) by the methods already described. On the other hand, if the two extracts contain compounds which will interact with the formation of an insoluble precipitate, they must be examined separately.

If the substance is not entirely dissolved by strong hydrochloric acid, it may consist of one of the few compounds which are only dissolved by *aqua regia*.‡ The residue is therefore treated with a small quantity of mixed nitric and hydrochloric acids, and boiled. The solution should be evaporated down in a porcelain dish until

* By the behaviour of the substance under this treatment, the presence of carbonates, sulphites, and peroxides will be indicated. Sulphur and silicic acid may be precipitated.

† See remarks on p. 187 with reference to this point.

‡ Such as sulphides of nickel, cobalt, mercury. The presence of these should have been indicated by the preliminary tests. The use of *aqua regia* should only be resorted to when absolutely necessary.

only a small bulk remains, in order to expel as much acid as possible, and then diluted with water; this solution may then be mixed with the hydrochloric acid extract.

(3) **Treatment of the Residue insoluble in Water or in Acids.**—The number of compounds insoluble in water and acids is very limited. Of commonly occurring substances, the following may be present—

(*a*) Sulphates of barium, calcium, strontium, and lead (the three last named being sufficiently soluble to be detected in the aqueous extract).

(*b*) Silica, and many natural silicates.

(*c*) Fluor spar, and other natural fluorides.

(*d*) Silver chloride (such insoluble silver compounds as the bromide, iodide, cyanide, and ferrocyanide are converted into the chloride by boiling with *aqua regia*).

(*e*) Oxides of aluminium and chromium (which have been strongly heated). Native stannic oxide (*tinstone.*)

(*f*) A few arsenates and phosphates. Carbon and sulphur.

These insoluble substances (except carbon and sulphur, which are readily recognised and require no further treatment) are converted into soluble compounds by fusion with alkali carbonates.* The insoluble residue (in the absence of lead and silver) is dried, and mixed with about four times its weight of fusion mixture and a little potassium nitrate, and fused in a platinum crucible until all effervescence is at an end. The crucible is then allowed to cool. [If the crucible be quickly chilled by standing it upon a piece of cold iron, *e.g.* the foot of a retort stand, or by dipping it on to the surface of cold water in a basin, the solidified contents of the crucible at once crack away from the metal, and can be removed as a solid cake, which can be broken up in a mortar.]

The fused mass is then boiled with water until nothing further dissolves, and filtered.

The *aqueous solution* is examined for such acids as in the

* If lead sulphate or silver chloride be present, they must either be removed, or the fusion must be conducted in a crucible of porcelain instead of platinum (in which case a certain amount of alumina from the crucible will pass into combination with the alkali carbonate). Lead sulphate may be removed by boiling the insoluble residue in a strong solution of ammonium acetate (the solution being tested for lead and for sulphuric acid). Silver chloride may be dissolved out by a solution of potassium cyanide; or it can be reduced to metallic silver by means of zinc (see Silver, reaction, p. 114), and after washing free from zinc chloride, the reduced silver can be dissolved in nitric acid. If sulphur be present in the insoluble residue, it may be expelled by heating the substance in a porcelain crucible.

nature of the case could be present—namely, sulphuric, silicic, hydrofluoric, chromic, arsenic, phosphoric, hydrochloric.*

The *residue*, after being thoroughly washed with hot water, until the wash-water is no longer alkaline, is dissolved in hydrochloric acid, and the solution examined for such metals as can be present.

In a few special cases, fusion with hydrogen potassium sulphate is resorted to instead of the fusion mixture above mentioned. This method is applicable, for example, in the case of minerals containing titanium, such as titaniferous iron ores (see pp. 73, 343).

* The fusion-mixture must obviously be free from sulphates, chlorides, etc., or tests for these acids are of no value.

CHAPTER XVII.

The Results of a Qualitative Analysis.

At the end of an analysis, the student will be in possession of the knowledge that the substance he has examined contained compounds of certain metals or positive radicals, and certain negative or acid radicals. If only one metal and one acid have been found, the substance must, of course, be the compound of these two; *e.g.* if magnesium and sulphuric acid have been detected, the compound must have been magnesium sulphate. If a metal has been found, but no acid radicals, the substance will in all probability be an oxide of that metal. In deciding this point, however, the student must consider the general properties of the substance, for if he finds, for example, the metal magnesium in a substance *soluble in water*, the compound obviously cannot be the *oxide*. He must therefore conclude that he has overlooked the acid radical.

When more than two metals and acid radicals are found in the substance, it becomes a much more difficult matter to discover which acid is in combination with which metal. Indeed, in many cases it is not possible to decide this point by a qualitative analysis alone. For example, suppose a mixture is found on analysis to contain the metals cadmium and sodium, and the acid radicals of sulphuric and nitric acids. Does the mixture consist of cadmium nitrate and sodium sulphate, or of cadmium sulphate and sodium nitrate? All the four salts are white, and none of them is so markedly different from the others in its solubility in water as to throw any light on the question; so that, if the two salts are present in fairly equal quantities, it is impossible to decide which pair of salts is present.

There are a number of points, however, which a student who cultivates his powers of observation will be able to note, which will often give a clue, if they do not afford proof, as to the manner in which the metals and acid radicals are united in a mixture.

For instance, even in such a mixture as the above, by carefully

noting the relative *quantities* of various precipitates obtained during the course of analysis, some light might be thrown on this point. Suppose it was noted that the amount of cadmium sulphide thrown down seemed very small, and that the test for sulphuric acid resulted in a most copious precipitation of barium sulphate, it would be fair to conclude that the cadmium was *not* present as sulphate.

Again, suppose barium and ammonium are the "metals" found along with the acid radicals of hydrochloric and nitric acids. The four possible salts are in this case also all of them white and easily soluble. If the salts are in fairly equal quantities, is it possible to decide how the acids and metals are distributed? If the *dry reactions* had been carefully observed, they would enable the student to decide the point. A mixture consisting of $BaCl_2$ and NH_4NO_3 when heated would melt, and give off water and nitrous oxide (decomposition of the ammonium nitrate), whereas if $BaNO_3$ and NH_4Cl were present, some of the ammonium chloride would at once sublime up the tube; and later on, brown fumes would appear, due to the decomposition of barium nitrate.

Very often two colourless and soluble salts contained in a mixture, undergo double decomposition with formation of a precipitate, as soon as water is added to the mixture with a view to its solution. When the precipitate is coloured (as would be the case, for example, if the mixture consisted of silver nitrate and sodium phosphate), the fact that it has been formed during the process of solution, and was not originally present, will be evident. On the other hand, when the product of interaction is also white, it is not always possible to decide this point. If such a mixture as silver nitrate and barium chloride be treated with water, the two soluble salts interact, with the precipitation of silver chloride. In this case a close inspection of the appearance of the mixture (the milkiness imparted to the water) would indicate that the substances were interacting. On the other hand, with a mixture such as barium chloride and magnesium sulphate, it would be almost impossible to say whether the *original mixture* contained barium sulphate or not.

When the substance under analysis is partly soluble in water and partly soluble in acids, it will be obvious that much information as to the distribution of the metals and acids will be gained, if each solution is separately examined. Thus, in a mixture consisting of lead carbonate and barium nitrate, water will remove the latter salt, and it becomes easy to settle that the lead, and not the barium, is in combination with the carbonic acid.

These are simple illustrations of the kind of evidence which has

to be made use of in ordinary qualitative analysis, when endeavouring to settle the question of the distribution of the metals and acid radicals. It will be obvious that the success with which the analyst will meet in this part of his work will largely depend upon the power which he possesses of seeing (*i.e.* of *observing*) all the various indications which are given him during the course of the analysis. The chief aim of the analytical student, as it should be the first object of his instructor, must always be the cultivation and development of these powers of exact observation. Without this, anylysis sinks into a mere dull mechanical routine, utterly devoid of all interest or educational value.

BOOK II.

QUANTITATIVE ANALYSIS.

PART I.

GRAVIMETRIC METHODS.

SECTION I.

PRELIMINARY MANIPULATIONS.

1. **Weighing.**—In gravimetric methods of analysis, as the name indicates, the quantities which it is the object of the analysis to determine, are estimated by the process of weighing. Not only is the amount of the material employed for analysis a *weighed* quantity (which may also be the case in *volumetric* methods), but the final products of the various processes are obtained in a form in which they also can be weighed. For instance, in making a quantitative analysis of, say, a silver coin, a weighed quantity of the metal will be operated upon, and the silver and copper will finally be obtained in the form of silver chloride and copper oxide. The exact quantities of these products will then be ascertained by the process of weighing, and from the weights so obtained the proportions of the two metals are deduced by calculation.

In order to obtain the accurate weight of a substance, it is necessary to employ a delicate balance, and to perform the operations of weighing with careful manipulation.

Fig. 15 represents a modern form of chemical balance. It is contained in a glass case with counterpoised sliding sashes, to exclude from it as much as possible, dust, damp, and laboratory fumes ;* and also to prevent disturbance due to air-draughts during the process of weighing.

* Unless circumstances render it unavoidable, the balance should never be kept in the laboratory. In all properly equipped schools a balance-room is provided, the instruments being placed where they will be subject to the least possible vibration, and never being moved.

The case is mounted upon levelling-screws, by means of which the instrument can be placed in a perfectly horizontal position, which is indicated by the spirit-levels attached to the base of the pillar.

When the balance is at rest, the beam and the scale-pans are held by the mechanical supports, which can be operated upon by means of the handle or "milled-head" placed outside and in front of the case.

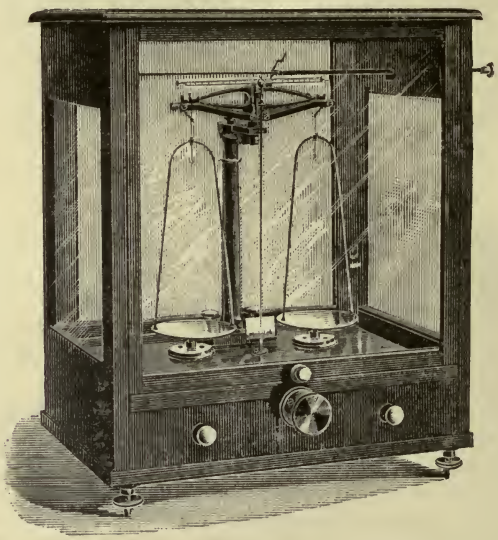

FIG. 15.

By a slight turn of the milled-head, these supports are simultaneously lowered, and the beam and pans are free to swing upon their "knife-edges."

The extent to which the beam swings is indicated by a pointer and scale; and if the balance is in proper order and adjustment, it will be seen that as the beam moves, the pointer travels practically an equal number of graduations in each direction.*

* If the pointer swings further in one direction than in the other, either the balance is not level, or is out of adjustment. The devices for adjusting the instrument differ with different balances. In the example shown in the figure, it is effected by means of the two little "bobs" which travel upon two screws attached to the ends of the graduated scale of the beam.

When not in use, the balance must never be left in this condition, but the supports must always be raised.

It is desirable to keep inside the balance case a glass jar about half filled with dry calcium chloride,* or fragments of quicklime, with a view to render the atmosphere of the case as dry as possible. This is especially necessary when any of the vital working parts of the instrument are made of steel instead of agate.

A set of gram weights, suitable for chemical analysis, is seen in Fig. 16. The weights from 1 gram to 50 grams (usually arranged to make up 100 grams in all) are of brass, while the fractions of the gram are flat pieces of platinium or aluminium foil. In practice it is usual to employ only the "deci" and "centi" grams of these small weights (*i.e.* the first and second places of decimals), and for the milligrams and fractions of a milligram (the third and fourth decimals) to use a sliding weight upon the beam of the balance. For this purpose the beam is graduated (in the figure, into tenths and hundredths), and the sliding weight, or *rider* (consisting of a piece of gilded brass wire, bent so that it can be placed astride the beam), is moved to any desired position on the beam by means of the carrier which passes through the side of the balance case. The weight of the rider is one centigram, and when it is placed on the tenth main graduation, its effect is the same as if it were placed in the scale, *i.e.* 10 milligrams or 1 centigram. The divisions of the beam, therefore, represent milligrams and sub-divisions of a milligram.

FIG. 16.

The weights must on no account be touched with the hand, but should be manipulated entirely by means of the forceps supplied with each set.

Great care should be taken in touching these parts, and it may be accepted as a general rule that the young student should not himself attempt the adjustment of the balance.

* The vessel should not be filled, especially when calcium chloride is used; as the salt becomes liquid by the absorption of moisture, and is likely to overflow the vessel. This is liable to happen when the balance is left unused for any lengthy period, as, for example, during a vacation.

It is essential that the weights all bear the exact relation to each other which is professed by the values indicated upon them; that is to say, the 1-gram must be exactly half the 2-gram weight, and this must be exactly a fifth of the 10 gram, and so on.* To ascertain that this is actually the case, they should be tested against each other—first by seeing that the several 1-gram weights are equal to each other; then that two of them exactly counterpoise the 2-gram; then that the 2-gram and the three 1-grams together equal the weight of the 5-gram, and so on.† When using the balance, the object to be weighed should be placed upon the left scale-pan, as it is more convenient for manipulation to use the right-hand pan for the weights (a left-handed operator will reverse this order).

Whenever anything (either objects to be weighed, or the weights) is put upon the scale or removed from it, the beam must be at rest on its supports.

The actual operation is conducted as follows: The article to be weighed, say a porcelain crucible with its lid, is placed upon the left scale-pan, the balance being at rest. A weight, which by a guess is judged to be rather greater than that of the object, is deposited by means of the forceps upon the opposite scale, and the beam gently liberated by turning the milled-head with the left hand. Suppose the 20-gram weight has been selected, and found too heavy; it is then removed, returned to its place in the box, and replaced by a 10-gram. If this is too little, the weight of the crucible lies between 10 and 20 grams. The 5-gram is then added, and if still insufficient, the 2-gram weight is added. If this is too much, the 2-gram is removed and a 1-gram substituted. If this is still too little, the weight of the object lies between 16 and 17 grams. The subdivisions of the gram are then used in the same systematic order, until the second decimal place is established, that is, until the whole number of centigrams is ascertained. Thus, suppose the weight is found to be between 16·74 and 16·75, the front sash is then closed, and the system brought into complete equilibrium by means of the rider, which is moved from division to division along the graduated beam, until the oscillation of the pointer is equal in both directions. Suppose that when this is the case, the position of the rider is midway

* It is not necessary, although it is preferable that it should be so, that the gram weight should be absolutely true to the standard gram, so long as all the weights used bear the correct ratios to each other.

† It is extremely rarely that the weights of a reliable maker, such, for example, as Oertling, are ever found to be untrue.

between the third and fourth main divisions, the weight of the crucible will then be represented by the number 16·7435 grams.*

In recording a weight, which should be done immediately the weighing operation is finished, the value of the weights should first be read off from the empty spaces in the box, and this should then be checked as the weights are returned one by one, beginning with the highest, to their respective compartments.

Except in the case of pieces of metal, alloys, etc., substances which have to be weighed must never be placed directly upon the scale-pan, but must be contained in a suitable vessel, such as a weighing-bottle or a watch-glass, which itself must be perfectly clean and dry.

The correct weight of an object cannot be taken while it is hot, owing to the disturbance introduced by the warm air-currents rising from it. Substances, therefore, which require to be heated previously to being weighed, must be allowed to cool down to the temperature of the air in the balance-room (see Desiccator, p. 196).

When taking a weighed quantity of a substance for analysis, it is usual to obtain its weight by *difference*. The prepared powder is contained in a light thin glass stoppered bottle (a convenient form of *weighing-bottle* is shown in Fig. 17), and the bottle with its contents is weighed.

Fig. 17.

A sufficient quantity of the powder is then carefully tipped out into the beaker or other vessel selected in which to operate upon the compound, and the bottle is again weighed. The difference between the two weighings represents the weight of the substance employed for the analysis.

Sometimes the clean empty vessel in which the substance is to be afterwards treated is itself weighed, then a quantity of the substance is introduced into it, and the vessel again weighed. This would be the method, for instance, when the substance is to be operated upon in a crucible.

2. **Drying and weighing a Filter.**—The filter-paper most suitable for use in quantitative analysis is a specially prepared Rhenish paper (Schleicher and Schüll, No. 589), which has been treated with hydrochloric and hydrofluoric acids in order to remove

* This method of weighing only gives the *absolute* weight of any object when the bulk or volume of the article is the same as that of the weights used to counterpoise it. In ordinary analytical operations, the difference between the weight of the air displaced by the objects and that displaced by the weights is too insignificant to be considered.

soluble mineral matters. The paper is obtained already cut into circles, the two most useful sizes for general use being respectively 9 and 11 centimetres (or, roughly, $3\frac{1}{2}$ and $4\frac{1}{2}$ inches) in diameter.

In certain quantitative estimations, as will be seen later, it is necessary to weigh a precipitate which has been dried upon a filter, and in such cases it is needful to know the weight of the dry paper itself, in order to deduct this from the total weight. The process of making this simple determination will form a useful exercise in a number of different operations which have constantly to be made in quantitative analysis.

The *apparatus* in which to weigh the filter may be either a light stoppered tube or weighing-bottle (A, Fig. 18), or a pair of watch-

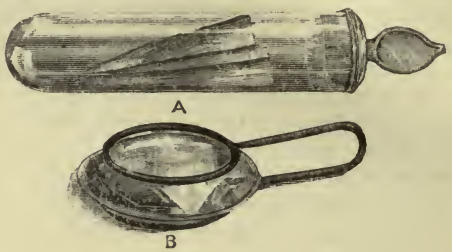

Fig. 18.

glasses with ground edges, held together by means of a bent wire clip (B, Fig. 18). A duplicate experiment may be made, using each of these forms of apparatus.

The bottle and the watch-glasses are first rendered perfectly clean by means of a dry clean glass-cloth, and are then made quite dry by being placed for about half an hour in a steam-oven; the bottle with its stopper out, and the glasses separated from each other.

The *steam-oven* consists of a double-walled copper vessel (Fig. 19), the space between the two walls being partly filled with water, which is maintained at the boiling temperature by means of a Bunsen lamp. In order to keep the water at a constant level, the oven may be provided with a feeding arrangement, shown at *f* in the figure. This consists of a syphon, the recurved end of which is constantly immersed in water, which is continuously flowing in at the bottom of the outer tube, and overflowing by the lateral tube into the sink.*

* In most well-appointed laboratories, stacks of steam-ovens, heated by steam from a steam-boiler, form a part of the regular fittings. The temperature within a steam-oven never quite reaches 100°.

The weighing-bottle and watch-glasses are placed upon the floor of the oven (which must be quite clean), or upon a piece of clean paper placed first upon the floor. At the expiration of about half an hour the apparatus is removed (the stopper being inserted in the bottle, and the glasses placed within the clip), and deposited in a desiccator, where it is allowed to cool.

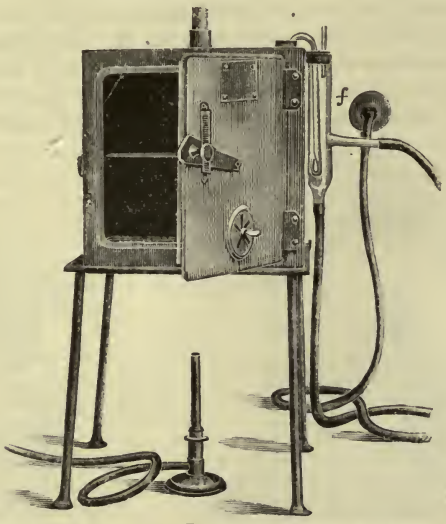

FIG. 19.

The *desiccator* is an air-tight glass vessel, in which the enclosed air is kept dry by means of some convenient drying agent, such as lime, calcium chloride, or sulphuric acid. In its most simple form, it may be an ordinary bell-glass with a ground edge, standing upon a thick piece of ground glass, over a glass dish containing the desiccating agent. The ground edge of the bell is greased with resin cerate, and the objects to be kept dry are supported upon a perforated zinc cover upon the inner dish (Fig. 20).

A handy form of desiccator, and one more easily carried about, is shown in Fig. 21. The desiccating material is placed in the lower part of the vessel, and a disc of perforated zinc, resting upon the shoulders, serves as a support for the objects to be dried. The whole is surmounted with a cover, ground to fit the vessel, which,

as in the other example, is greased with resin cerate.* When the apparatus has cooled in the desiccator, it is next carefully weighed, the weight of the empty tube and that of the watch-glasses being separately noted.

Two of the filter-papers are now folded in the usual manner. One of them is then rolled loosely, and introduced into the weighing-bottle ; the other is carefully folded, *without cracking the paper* (because in actual work it would afterwards be used for filtering), so that it can be placed between the watch-glasses. Each piece of apparatus with the enclosed filter is then weighed. The former weights deducted from those now obtained, give the weights of the *undried* filters. The weighing-bottle and the glasses (opened

FIG. 20.

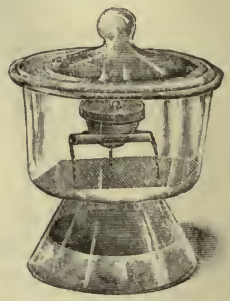

FIG. 21.

as before) are then replaced in the steam-oven, and heated for half an hour, after which they are returned to the desiccator to cool, and then re-weighed. The difference between the *first* weights and these last is the weight of the *dried* filters.

By comparing the weights of the undried and the dried filters, the actual weight of the moisture which such a piece of filter-paper is capable of absorbing from the atmosphere will be ascertained.

The tube and watch-glasses should be once more heated for

* Resin cerate, as supplied by the shops, is often rather too stiff. It is well in this case to melt a quantity of it in a porcelain dish, and add a little vaseline to it. The whole should then be poured into a clean vessel to cool. An ordinary ointment pot with a cover (such as the druggists use) is a convenient vessel in which to keep it. Dust and dirt should not be allowed to get into it, as any small particles of gritty matter will prevent the lid of the desiccator from closing quite air-tight.

a similar period, cooled as before in the desiccator, and again weighed. The weights now obtained should be concordant with the last; if they are not, the heating must be repeated until two consecutive weighings are found to agree.

In actual practice we do not want to know the weight of the moisture expelled from the filter, or even the weight of the dry paper alone. It is enough to know the weight of the dry paper and the weighing-bottle. The process is therefore reduced to a single operation. The paper is placed in an unweighed bottle, and after half an hour's drying, it is cooled in the desiccator and weighed. The paper is then used to receive the precipitate which has to be weighed. Then, after proper treatment, the filter with the precipitate upon it is returned to the same weighing-bottle and heated in the steam-oven for a suitable time, after which it is allowed to cool in the desiccator and weighed; the process of heating and weighing being repeated until two concordant weights are obtained. The weight of the bottle *plus* paper deducted from the weight of the bottle *plus* paper *plus* precipitate, gives the weight of the precipitate, which it is the object of the series of operations to ascertain.

Most substances, especially when in the state of fine powders, are more or less hygroscopic. On exposure to the air, they absorb and retain a certain amount of moisture. Some things—such, for example, as copper oxide, manganese dioxide, charcoal powder, etc., are able to absorb in this mechanical way very appreciable quantities of moisture. The water so retained is in almost all cases entirely expelled by heating the substance for a suitable time in the steam-oven, after which, in order to preserve it in its dry state, it must be kept in the desiccator.

When the amount of moisture such substances contain has to be estimated, a convenient quantity (from 2 to 10 grams, depending upon the amount of moisture) is weighed out into a pair of watch-glasses, and the process conducted in the manner above described in the case of the filter-paper. If the substance is one which cannot withstand a temperature of 100° without suffering chemical decomposition, other methods have to be adopted for estimating the moisture it contains, which will be described later.

3. **Estimation of Water of Crystallisation.**—Most salts containing water of crystallisation readily part with some or all of their water when moderately heated. In those cases where the salt suffers no other change in composition at the temperature necessary for the expulsion of the water of crystallisation, the latter may be estimated by ascertaining the loss of weight which results from heating the substance. If the salt loses its water of crystallisation

at or below the temperature of 100°, the operation may be conducted in the steam-oven in the manner described above ; but when higher temperatures are necessary, an air-oven is employed.

The *air-oven* (Fig. 22) is similar in construction to the steam-oven, except that it contains no water between the walls. (The oven is frequently only a single-walled copper chamber, fitted with a shelf or false bottom). It is heated by a Bunsen flame, and the

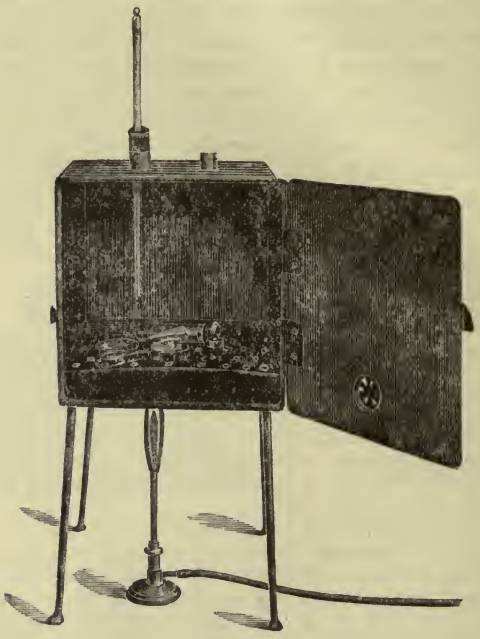

FIG. 22.

temperature of the air within is ascertained by means of a thermometer, which passes through the top by means of a cork. The door of the oven is usually furnished with a ventilator, which can be opened or closed in order to regulate the current of air through the oven ; the escaping air passes out through a second opening in the top.

The objects to be heated must be placed upon the perforated shelf (or upon any other convenient support), which is at some

considerable distance from the bottom of the oven, and the bulb of the thermometer should be as near to the object as possible. Articles to be heated must not be placed directly upon the floor of the oven, as obviously the metal of that part of the oven will be hotter than the temperature indicated by the thermometer. This is more especially the case when the oven is a single-walled apparatus.

Within reasonable limits, it is easy to maintain the temperature of such an oven at any desired point by regulating the Bunsen flame. As the mercury in the thermometer rises nearly to the required point, the lamp is gradually turned down until the upward movement of the mercury ceases. If this point is above the desired temperature, and if after a few minutes it does not fall, the flame should be lowered still more. (Thermostats, or instruments which serve as gas-governors, can be fitted to the air-oven, so that the supply of gas necessary to maintain the oven at a constant temperature is automatically regulated.)

Crystallised copper sulphate may be conveniently used in order to illustrate the method of determining water of crystallisation. This compound crystallises with five molecules of water. Four of these it gives up slowly at 100°, but more rapidly at 110°, while the remaining molecule is retained until the temperature has risen above 200°. In the following exercise, each of these proportions of water will be separately determined.

A quantity of purified copper sulphate is coarsely powdered in a mortar as quickly as possible, and the powder placed in a stoppered bottle (a slight loss of water will result if the powdering process involves a prolonged exposure of the salt to the air). About two grams of it are then weighed out into a pair of watch-glasses and clip, by first weighing the clean dry glasses and clip, and then placing into them a quantity of the salt which is judged to be about two grams, and weighing again. The glasses are then separated, and placed upon the shelf of the air-oven, the latter being maintained at a temperature between 110° and 115°.

At the expiration of an hour the glasses are removed from the oven, quickly put together in the clip, and allowed to cool in the desiccator, and then weighed.

They are then returned to the oven and reheated for about half an hour, after which they are again taken out and cooled and weighed. If this last weight differs appreciably from the previous one, the process must be repeated until the weight is constant.

From these data the percentage of water lost by heating the salt to 110°–115° is calculated in the manner shown in the following example :—

	Grams.
Weight of watch-glasses and salt	17·3465
,, ,, empty	15·1890
Weight of copper sulphate used	2·1575
Weight of watch-glasses and salt after first heating	16·7545
,, ,, ,, second ,,	16·7230
,, ,, ,, third ,,	16·7230
Weight of glasses and original salt	17·3465
,, ,, dried ,, ...	16·7230
Weight of water lost	0·6235

Since 2·1575 grams of salt lost 0·6235 gram of water—

then $\frac{0{\cdot}6235 \times 100}{2{\cdot}1575} = 28{\cdot}90$ = percentage of water lost at 110°–115°

The calculated percentage for four molecules of water = 28·91

therefore the error, as deficit, = 0·01

The temperature of the air-oven is now raised to between 210° and 215°, and the opened watch-glasses with the salt are again heated for about an hour to this higher temperature. The glasses are then removed, cooled in the desiccator and weighed. As in the former case, this is repeated until two consecutive weighings agree.

In the example the following weights were obtained :—

	Grams
Weight of glasses and salt after first heating to 215°	16·5685
,, ,, ,, second ,,	16·5680
Weight of glasses and original salt	17·3465
,, ,, dried ,, ...	16·5680
Total weight of water lost	0·7785

Since 2·1575 grams of salt have lost 0·7785 gram of water–

then $\frac{0{\cdot}7785 \times 100}{2{\cdot}1575} = 36{\cdot}08$ = percentage of water lost at 215°

Percentage calculated for five molecules of water of crystallisation } = 36·14

Error, as a deficit, = 0·06

In determining the water of crystallisation of salts which undergo no other chemical change, except the loss of their water, even when heated to a high temperature, it is more expeditious to

heat the salt in a crucible by means of a small Bunsen flame. Copper sulphate could not be treated in this way, as at a temperature somewhat over 300° the anhydrous salt suffers decomposition. A convenient salt with which to illustrate the method is barium chloride, which crystallises with two molecules of water.

A crucible (preferably of platinum) with its lid, is first heated upon a pipeclay triangle (as shown in Fig. 23) for a few minutes, and weighed after cooling in the desiccator.

Into the crucible a quantity of pure, powered barium chloride is introduced, and the weight again taken.

The weight of salt taken should be between two and three

FIG. 23.

grams.* The crucible is at first gently heated by a small Bunsen flame, the lid being upon the crucible. The temperature is gradually raised until the crucible attains a low red heat, at which

* The quantity of material taken for an estimation must depend upon several considerations. Speaking generally, the smaller the weight employed, the more expeditiously will the analysis be made. At the same time, errors due to experiment will be more magnified, and therefore a greater demand is made upon the manipulative skill of the analyst. The relation between the weight of the substance which is to be estimated, and the formula-weight of the compound to be analysed has also to be considered; for instance, in the present case, owing to the high atomic weight of barium, and the comparatively small quantity of water present, the weight of the latter constitutes only a small part of the total formula-weight of the crystallised salt.

it is maintained for about ten minutes. It is then placed in the desiccator to cool, and afterwards weighed.

The operations of heating and weighing are repeated until the weight is constant. The following is an example :—

	Grams.
Weight of platinum crucible and salt	47·6275
,, ,, alone	45·3640
Weight of barium chloride taken	2·2635
Crucible and salt after first heating	47·2950
,, ,, second ,, ...	47·2940
Weight of crucible and original salt	47·6275
,, ,, dried ,, ...	47·2940
Weight of water lost	0·3335

Since 2·2635 grams of salt contained 0·3335 gram of water—

then $\frac{0{\cdot}3335 \times 100}{2{\cdot}2635}$ = percentage of water of crystallisation = 14·73

Percentage calculated on the formula $BaCl_2,2H_2O$ = 14·75

Error, as deficit, = 0·02

In cases where the substance undergoes other chemical changes at, or near, the temperature at which it parts with its water of crystallisation, or with the moisture which is mechanically retained by it, the weight of the water which it gives up cannot be estimated by *loss*. The method is therefore so modified that the expelled water is absorbed by calcium chloride, or other suitable desiccating material, which is accurately weighed before and after the experiment. The gain of weight thus observed represents the weight of water absorbed. The apparatus for carrying out the method is shown in Fig. 24.

A weighed quantity of the substance is heated in the bulb-tube B. By means of an aspirator, a slow stream of air (dried by passing through the calcium-chloride tube A) is drawn through the bulb, and the water-vapour which is being expelled is absorbed in the weighed calcium-chloride tube D. The wash-bottle W, containing sulphuric acid, serves to show the rate at which air is being drawn through the apparatus, and also prevents the drying-tube D from absorbing water-vapour from the aspirating arrangement.

Fitting up the Apparatus.—The two drying-tubes are first perfectly cleaned and dried, and provided with tight-fitting corks *

* When ordinary corks are employed in fitting up apparatus generally, those having a fine, close texture and free from faults should alone be used.

(either ordinary or caoutchouc) carrying tubes as shown in the figure. They are then nearly filled with dry granulated calcium chloride, the pieces of which should be about the size of grains of wheat. Powder must not be put into the tubes, or they will be liable to become blocked; therefore, if the stock of calcium chloride contains much that is too fine for the purpose, it may be passed as quickly as possible through a warm dry wire sieve. A little plug of cotton-wool is loosely pushed down upon the top of the calcium chloride, and the tubes securely closed by the corks.

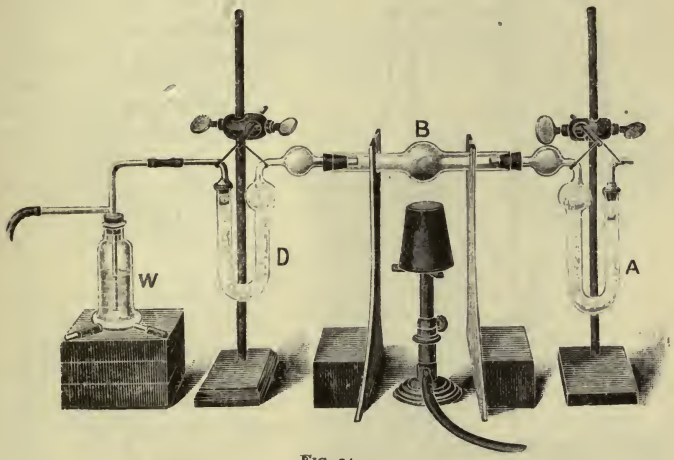

FIG. 24.

In the case of the tube D, a little plug of cotton-wool is first introduced, and drawn round to the top of the bulb by applying suction to the end of the narrow tube, in order to prevent particles of the calcium chloride from getting into the narrow tube. The cork which closes the open limb of this tube should be cut off close to the glass with a sharp knife, and the surface completely covered by shellac or sealing-wax. This prevents the cork from absorbing moisture from the air.

The cork should be at first a trifle too large for the tube it is intended to fit. It is then carefully pressed in cork-squeezers, or rolled under the foot with a gentle pressure, which will both soften it and make it a little narrower. The hole should be cut with a sharp, clean cork-borer to the exact size required to tightly fit the tube which it is intended to pass through it, without having to use a round file to enlarge it.

The ends of the exit tubes are closed by means of little caps, made by plugging one end of a short piece of caoutchouc tube with a piece of glass rod. These caps should remain on the tubes except when they are actually being used, or being weighed. The tube D, which has to be weighed, is furnished with a loop of wire (preferably platinum), by means of which it can be suspended from the arm of the balance. The two drying-tubes are attached to a hard glass bulb-tube by means of rubber or ordinary corks in the manner shown in the figure. If ordinary corks are used, they should first be thoroughly dried in the steam-oven. A simple form of aspirator for small pressures is shown in Fig. 25. An ordinary T-tube is attached to a narrow glass tube about 70 cm. long, which has been bent into a loop near one end. When a gentle stream of water from the tap is allowed to enter through the tube S, air is drawn in through the other limb of the T-tube and carried down the long tube. By means of the clamp D, the rate at which air is drawn through the apparatus can be regulated. During the experiment it should be such that the bubbles pass through the sulphuric acid in the little wash-bottle W about two per second.

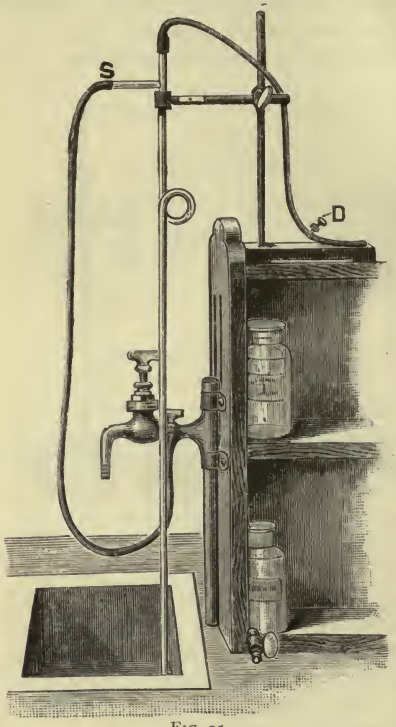

FIG. 25.

To carry out the Operation.—The drying-tube D is first carefully weighed, *without the little caps* which close the ends. These are instantly replaced as soon as the weight is ascertained. The bulb-tube, after being carefully wiped and dried, is weighed, and a suitable quantity (2 to 4 grams) of the substance is introduced into the bulb. This may be accomplished by placing the powdered

substance upon a strip of writing-paper, folded into a gutter sufficiently narrow to pass into the tube (A, Fig. 26), and depositing it in the bulb by twisting the paper (B, Fig. 26). Before withdrawing the paper, it should be turned over again into its original position, so that on its way out it may not leave any traces of the powder in the stem of the bulb. The bulb is now re-weighed, the increase being the weight of the substance taken.

The two U-tubes are then attached to the bulb, the caps being removed only from the extremities which are fitted to the bulb-

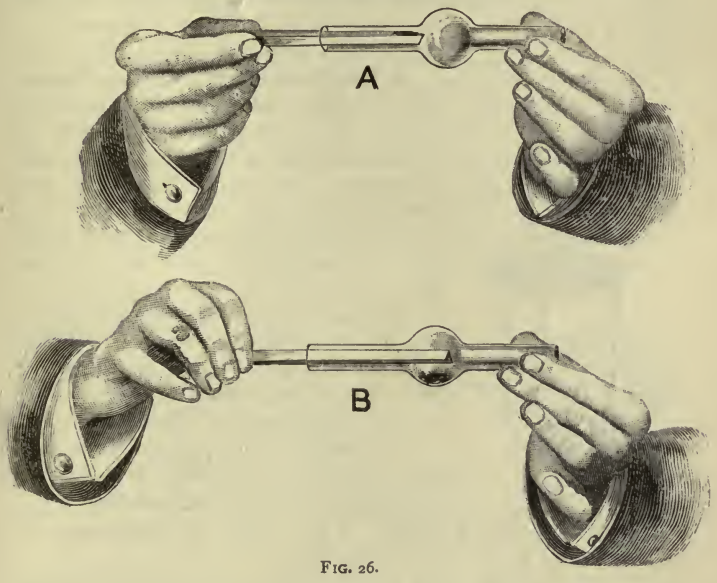

FIG. 26.

tube. The aspirator is then set in operation, and when the rate at which it draws air through the acid in bottle W is adjusted to the requirements of the experiment, the caps are removed from the drying-tubes, and the bottle W is attached by a narrow caoutchouc tube to the drying-tube D. Two screens, made of asbestos cardboard, are placed in the position shown in the figure to shield the corks and the drying-tubes from the heat of the lamp.

The bulb is gently heated by means of a small Bunsen flame, the temperature being gradually increased until the whole of the water is expelled. Some of the moisture will be seen to condense

upon the stem of the bulb-tube, but as the heated air passes through the apparatus, this gradually vaporises and passes on into the absorbing-tube D. When the whole of the water has been expelled, tube D is detached and re-weighed. Its gain in weight represents the amount of water contained in the weighed amount of the original compound.

When it is desirable to heat the substance to some definite temperature, the bulb-tube is replaced by the U-tube (Fig. 27), which can be heated to the required temperature in a bath of oil or melted paraffin, the temperature being ascertained by a thermometer suspended in the bath.

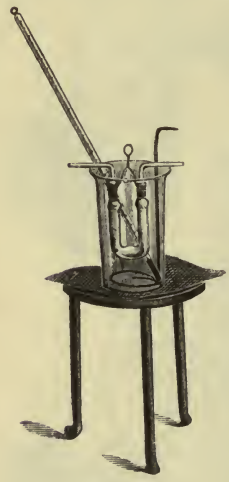

Fig. 27.

4. **Determination of the Weight of the Filter-ash.**—In the majority of cases, before a precipitate is weighed, it is necessary that it be subjected to a high temperature. It has, in fact, often to be strongly heated in a crucible, in order to convert it into a product suitable for weighing. For example, the precipitate may consist of a hydrated oxide (perhaps of indefinite composition) which it is necessary to convert into the oxide (having a known and definite composition) by the action of heat. In such a process, obviously, the paper becomes burnt up, and the ash only is weighed. It is therefore needful to know what is the weight of the ash so produced, that it may be deducted from the total weight.

For this purpose a number of the papers are incinerated one after the other in the following manner :—

A clean crucible, with its lid (either a platinum or porcelain crucible may be used), is supported upon a pipeclay triangle (Fig. 23), and heated by means of a Bunsen flame for a few minutes. It is then allowed to cool in the desiccator, and weighed. One of the filters is then folded as shown (*a*, Fig. 28), and rolled into a compact little bundle (*b*). A piece of moderately stout platinum wire is then wound a few times round it, leaving a sufficient length of wire to serve as a handle,* as shown at *c*. The

* If, as is sometimes recommended, the wire is fused into a glass tube for a handle, the greatest care must be taken to prevent any little fragments of glass, which are liable to chip off by the bending of the wire, from falling into the crucible.

crucible is then placed upon a clean sheet of white paper (or upon a square of glass standing on white paper), with the lid by its side.

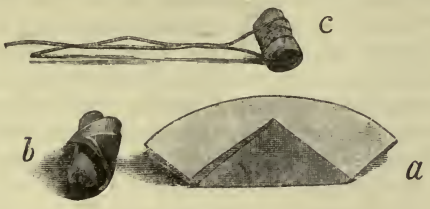

FIG. 28.

The rolled-up paper, being held over the crucible as in Fig. 29, is then ignited (set fire to) by means of a Bunsen flame. After the flame of the burning paper has died out, the charred and shrunken remains still smoulder on for some time, until the carbon has burnt away and a grey mass is left. It may be lightly touched once or twice with the Bunsen flame (it must not be held for any length of time in the gas-flame), and then allowed to drop into the crucible.

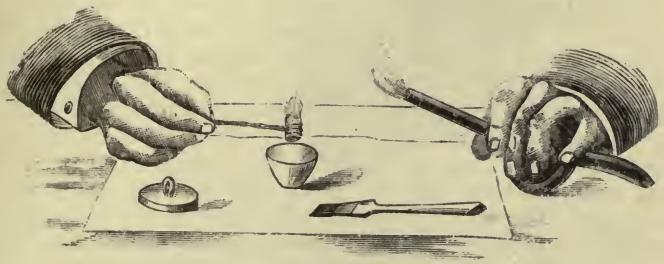

FIG. 29.

If the ash does not easily fall away from the wire as the latter is inclined over the open vessel, a gentle tap of the wire against the rim of the crucible will usually detach it.

This process is repeated (two papers may be burnt at a time), until the ash from ten filters has been obtained. If any minute particles have fallen on to the paper or glass, they are carefully swept up into the crucible with a small camel's-hair brush or a feather. The crucible is then covered, heated again for a few minutes as at first, placed in the desiccator to cool, and weighed. The increase in weight is the weight of the ash from ten filters, and by dividing the result by ten, the average weight of the ash of

one is obtained. If the filters mentioned on p. 193 are used, the weight of the ash they yield is indicated on the packets ; the student will therefore be able to compare the result of his determination with the figure there given. It will be obvious that the larger the number of papers incinerated, the more distributed will be the experimental errors, and therefore the more exact will be the result.

5. **Preparation of Pure Salts.** — In order to test the accuracy of the results of a quantitative analysis, two courses are open. Either duplicate analyses are made, so that two concordant results may be obtained ; or the result of a single analysis is compared with the calculated theoretical composition of the compound under examination. It will be obvious that it is only when compounds of known composition and of known purity are being analysed that the latter plan is possible ; in all professional work the former method is necessarily adopted. For the student, however, who is beginning the practical study of quantitative methods, it is advantageous that his first exercises in quantitative estimations should be made with salts which are practically pure compounds. Purified salts (*i.e.* salts which have been so far purified that the amount of impurity present is too small to appreciably affect the analysis) are readily obtained from chemical manufacturers, but it is well for the student himself to prepare some of the compounds he will use, in order that he may gain experience in the general methods employed for this purpose.

1. *Crystallisation.*—By the process of crystallisation from a suitable solvent (repeated several times, if necessary), a salt may be separated from most soluble substances with which it is admixed. The wider the difference between the solubilities of the substances to be separated, the more easily is purification by this method effected ; *e.g.* barium chloride is more readily freed from calcium chloride by recrystallisation than from potassium chloride, the solubility of the latter salt at the ordinary temperature being only slightly different from that of barium chloride, while calcium chloride is an extremely soluble salt.

Certain salts, on the other hand, cannot be separated from each other by the process of crystallisation ; because when the solution containing them is allowed to crystallise, the two are together deposited, not as a mere mixture of crystals of the two individual compounds, but in the form of a double salt, having a definite composition.

The operation of recrystallising a salt is similar in outline in every case, with certain differences in detail.

A hot strong solution of the commercial salt is made in water. For this purpose a quantity of water, say from 200 to 300 c.c., is heated in a beaker, either by means of a rose burner, the beaker being supported upon wire gauze as in Fig. 30, or by means of a small Fletcher's burner (Fig. 31), which is a convenient lamp and stand in one. A quantity of the salt to be recrystallised is then added, moderate portions at a time, until a tolerably strong solution is obtained. The quantity of salt which will be dissolved will depend obviously upon the solubility of the compound operated

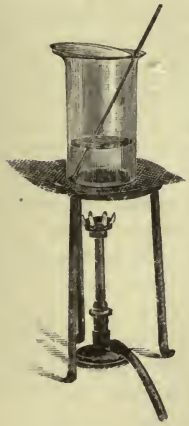

FIG. 30.

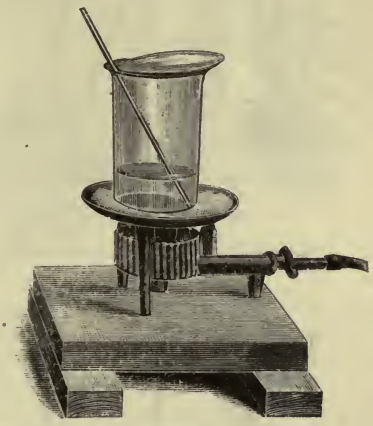

FIG. 31.

upon; but it is sometimes necessary to take other considerations into account in fixing a limit to the strength of the solution which is made. For example, zinc sulphate and magnesium sulphate, when deposited from solutions at a temperature below 40° and 50° respectively, form crystals containing seven molecules of water; but if the crystals are deposited from solutions above these temperatures, they not only have a different form, but contain only six molecules of water of crystallisation. Therefore the solution must either be of such a degree of concentration that crystals do not form until the temperature has fallen to these degrees, or else the temperature of the water in which the salt is dissolved should not be higher than these points.

Unless the solution is absolutely clear and bright (which, with the ordinary commercial salts, will hardly ever be the case), it

must be freed from suspended impurity by filtration. In order to prevent the solution from crystallising in the funnel, and so blocking the filter, it is necessary to keep the funnel warm during the operation. This may be done by inserting the funnel in a double-walled metal jacket, made in the shape of a truncated cone. The jacket contains water which is heated by means of a Bunsen flame (Fig. 32). The same result may be accomplished by winding a piece of lead or "compo" pipe round the funnel, two or three turns being enough, and blowing steam

Fig. 32.

Fig. 33.

through the pipe. The steam may conveniently be generated in a common tin can. The arrangement is shown in Fig. 33.

A still simpler plan for keeping the funnel warm is shown in Fig. 34. A short piece of "compo" pipe is closed at one end, and bent at that end into a loop or ring. Five or six pinholes are bored in the ring, and the pipe is supported by means of a clamp, so that the ring is at some little distance below the body of the funnel. The pipe is connected to the gas-supply, which is regulated so that little beads of flame are burning at the holes in the pipe.

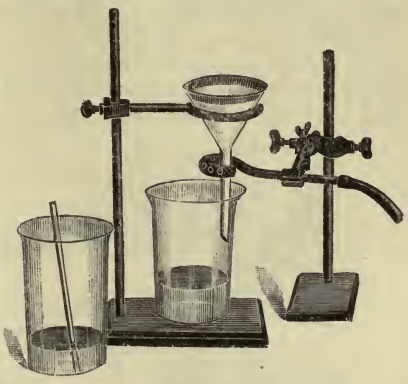

Fig. 34.

The beaker containing the filtered solution is then placed in a basin or other convenient vessel containing cold water, in order to cool the liquid as quickly as possible. The solution is also continually stirred with a glass rod. In this way the salt is deposited in the form of very small crystals, whereas if allowed to cool slowly and to be undisturbed, the crystals would be larger and better defined. In the former condition the salt is more easily freed from the mother-liquor.

When the solution is cold, the crystals are allowed to settle, and the mother-liquor decanted off. The residue is then transferred to a drainer, which is a circular disk of porcelain or glass, perforated with a number of small holes, and supported in a glass funnel. In this way the greater part of the mother-liquor is separated from the crystals. The process is accelerated by partially reducing the atmospheric pressure beneath the funnel. For this purpose the stem of the funnel is fitted into the mouth of a stout conical flask by means of a perforated caoutchouc stopper, and the branch tube of the flask is connected to any suitable exhausting apparatus, such as a Geissler's or Wetzel's water-pump. The arrangement is shown in Fig. 35, where a Wetzel's water-pump is represented, which is one of the best forms of its kind. Between the pump and the filtering-flask an empty Woulff's bottle should intervene, with the tubes arranged as shown. The object of this is to intercept the water which is sucked back from the pump towards the flask, when the pump is stopped while there is still a

partial vacuum in the apparatus. The water which is thus driven into the Woulff's bottle, is automatically drawn out again when next the pump is set in action. The rubber tube used for the water-supply must be canvas-covered or canvas-lined, in order to withstand the water-pressure; that employed for the other connections must be sufficiently thick in the walls to resist the pressure of the atmosphere, without collapsing.

In cases where the crystals are only moderately soluble in cold water, they may be rinsed while upon the drainer by pouring a little cold water upon them. After they have been allowed to

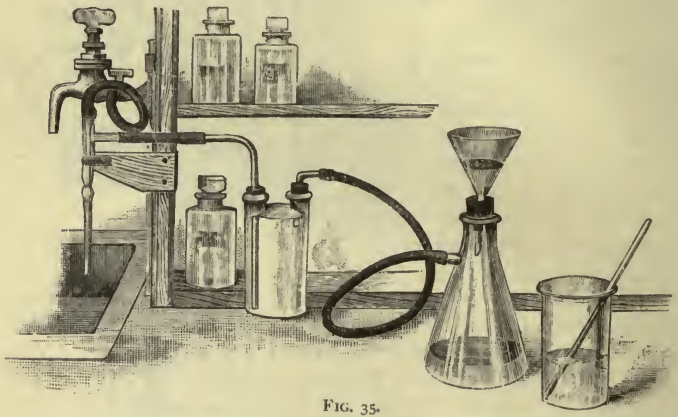

FIG. 35.

drain as completely as possible in the funnel, they are then spread out upon a clean porous plate * or tile to dry.

If the salt being operated upon is one which does not effloresce or undergo any change on exposure to the air, it may be left until quite dry, care being taken to prevent particles of foreign matter from falling upon it. In the case of compounds which cannot safely be exposed so long, the crystals are finally dried by gently pressing them between folds of filter-paper. When dry, the crystals should be transferred to a dry stoppered bottle.

After this manner, any of the following salts may for practice

* Porous plates are most convenient for the purpose, and are cheaper than the tiles. They are ordinary plates which, on account of some imperfection or slight damage, are not worth carrying any further in the process of manufacture than the "biscuit" or unglazed stage. A porous plate (or tile) must not be used a second time (unless for another crystallisation of the same salt), as it would obviously introduce impurities into the compounds being dried.

be recrystallised : $CuSO_4,5H_2O$; $MnSO_4,5H_2O$; $ZnSO_4,7H_2O$; $NiSO_4,7H_2O$; $MgSO_4,7H_2O$; $BaCl_2,2H_2O$; KCl ; NH_4Cl ; K_2CrO_4 ; $K_2Cr_2O_7$.

Double salts are salts which contain two metals and only one acid radical.* They are usually formulated as associations of molecules of the two single salts which enter into their composition : thus, potassium aluminium sulphate (potassium alum), $K_2SO_4,Al_2(SO_4)_3,24H_2O$; ammonium nickel sulphate, $(NH_4)_2SO_4,NiSO_4,6H_2O$; potassium magnesium sulphate, $K_2SO_4,MgSO_4,6H_2O$; and so on.† The exact nature of the union between the molecules of the two single salts is not known, but it is a union which exhibits shades of stability just as in the case of that which exists between the atoms within the molecules. For instance, the union between the two sulphates in potassium alum is a much closer or more stable union than that between the two sulphates in potassium magnesium sulphate. When alum is dis-

* Although it is true that "double salts" contain two metals and one acid radical, it does not follow that all salts which contain two metals and one acid radical belong to this class of compounds. For instance, *microcosmic salt*, $HNa(NH_4)PO_4$, and ammonium magnesium phosphate, NH_4MgPO_4, are examples of salts containing *two* metals (regarding NH_4 as a metal) and *one* acid radical, which are not classed as "double salts." Strictly speaking, a compound is only a "double salt" when the sum of the effective valencies of the two metals is not greater than the basicity of the single acid radical. Thus, the basicity of the acid radical (PO_4) is 3. In *microcosmic salt* the sum of the valencies of the two metals Na and (NH_4), is only 2, while in ammonium magnesium phosphate it is 3. On the other hand, in such a compound as ferrous ammonium sulphate, $(NH_4)_2SO_4,FeSO_4,6H_2O$, which is a true double salt, the sum of the valencies of the metals present is 4 (two monovalent NH_4 groups and one di-valent iron), while the single acid radical (SO_4) has a basicity only of 2.

† Some chemists adopt formulæ which are constructed on the model of the formula of a single salt ; thus, alum is represented as $Al_2K_2(SO_4)_4,24H_2O$, ferrous ammonium sulphate as $Fe(NH_4)_2(SO_4)_2,6H_2O$; and so on. The use of formulæ of this type, however, is more advantageously reserved for a special class of double salts, which differ from those here mentioned in their behaviour towards reagents in a very marked manner. For example, if barium chloride be added to a solution of either of the double sulphates mentioned above, *all* the sulphuric acid radical is precipitated as barium sulphate, while chlorides of both metals are formed ; thus—

$$K_2SO_4,Al_2(SO_4)_3 + 4BaCl_2 = 4BaSO_4 + 2KCl + Al_2Cl_6$$

Certain double salts, however—such, for instance, as the double chlorides of platinum and the alkali metals—do not behave in this way. Thus, if silver nitrate be added to a solution of sodium platinic chloride, $2NaCl,PtCl_4$, the whole of the chlorine is *not* precipitated as silver chloride; the silver is only capable of uniting with 2 out of the 6 atoms of chlorine in the compound, the result being the production of the compound $2AgCl,PtCl_4$ and two molecules of $NaNO_3$. Such a compound as this may with advantage be expressed by the formula Na_2PtCl_6, and the action of silver nitrate may be indicated by the equation—

$$Na_2PtCl_6 + 2AgNO_3 = 2NaNO_3 + Ag_2PtCl_6$$

solved in water (without entering upon the much-debated question as to the condition of the salt *while in solution*), the solution, on evaporation, again deposits the double salt unchanged; but when the double potassium magnesium sulphate is similarly treated, the salt undergoes a partial separation, and the crystals which are deposited consist partly of the double salt and partly of the least soluble of the two single salts, namely, the potassium sulphate.

These facts have to be kept in mind in the preparation or purification of double salts, for it is obvious that, while the more stable of this class of compounds (such as alum) can be purified by recrystallisation, the process is inadmissible in the case of those salts which readily separate into the simple salts of which they are composed. The general method for the preparation of double salts is to take the two single salts in the proportion of their formula-weights, make a strong solution of each separately in water, and carefully mix the two liquids. For example, to prepare potassium alum, the two salts, aluminium sulphate, $Al_2(SO_4)_3,18H_2O$ (formula-weight = 612), and potassium sulphate, K_2SO_4 (formula weight = 174), are taken in the proportions indicated by these weights. (A suitable quantity in this case would be one-third of these numbers in grams, *i.e.* 204 grams of aluminium sulphate and 58 grams of potassium sulphate.) If the salts are both pure (so called) compounds, the weights employed may be as near to the theoretical proportions as will be obtained by weighing the salts on a rough balance. If, however, ordinary commercial salts are used, a slight excess of aluminium sulphate should be taken, as this is likely to be the less pure of the two compounds. The two salts, in separate beakers, are dissolved in hot water, and the solutions filtered if they contain any suspended impurities. A slight loss of the salts may occur in this operation, but by using moderately small filters, and exercising care, the loss will be practically equal in both cases. The two clear solutions are then thoroughly mixed by pouring them from one beaker to the other once or twice, carefully avoiding any loss of either liquid. The solution is then cooled, and the crystals drained and dried in the manner already described.

In those cases where the union between the two component salts in the double compound is less stable, as already mentioned, the more insoluble of the single salts is liable to crystallise out in greater or less quantity along with the double compound. To prevent this, a considerable excess of the *more soluble ingredient* must be employed; usually an excess equal to one-fourth or one-

third of the formula-weight is employed. Thus, in the case of the double potassium magnesium sulphate above cited, instead of 246 (the formula-weight of $MgSO_4,7H_2O$) and 174 (formula-weight of K_2SO_4), the proportions used should be 246 + 80 to 174.

In special cases—such, for instance, as the double salts containing ferrous sulphate as one of the components—the separate solutions must be made at temperatures lower than the boiling-point, in order to guard against the precipitation of basic salts. Thus, in preparing ferrous ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, the temperature of the solutions should not be higher than about 40° C.

The two salts are taken in the proportion of their formula-weights ($FeSO_4,7H_2O = 278$, and $(NH_4)_2SO_4 = 132$), and dissolved in water so as to obtain solutions as strong as possible at a temperature of about 40°. The liquids are then mixed, and the mixture acidified by the addition of two or three drops of dilute sulphuric acid. The solution is then cooled and crystallised as usual.

For practice, such double salts as the following may be prepared : $NiSO_4,(NH_4)_2SO_4,6H_2O$; $MnSO_4,K_2SO_4,6H_2O$; $2(NH_4)Cl,CuCl_2,2H_2O$.

Precipitation by Change of the Solvent.—Salts may be thrown out of their aqueous solution by the addition to the liquid of some substance which is miscible with, or soluble in, the water, but which, when so dissolved or mixed, constitutes a solution in which the salt previously dissolved in the water is insoluble. For instance, barium chloride is soluble in water but is almost insoluble in a solution of hydrochloric acid in water. If, therefore, hydrochloric acid be added to such an aqueous solution, the barium chloride is at once thrown out of solution as a fine crystalline precipitate.

Again, ferrous sulphate is soluble in water, but practically insoluble in alcohol. By adding alcohol, therefore, to an aqueous solution of this salt, a precipitate of ferrous sulphate in fine powder is produced.

As illustrations of this method, the following exercises may be made :—

(1) *Precipitation of Sodium Chloride by Hydrochloric Acid.*—About half a litre of water is saturated with common salt, and the brine filtered.* Into the clear solution, contained in a beaker, a

* As salt is almost equally as soluble in cold as in hot water, the liquid need not be heated ; and for the same reason, should occasion arise where a hot solution of salt has to be filtered, there is no necessity to use the steam-jacket for the funnel.

stream of gaseous hydrochloric acid is passed. The gas is generated by acting upon common salt with sulphuric acid (previously mixed with water in the proportion of 11 volumes of strong acid to 8 of water, and the mixture cooled) in the flask H, Fig. 36. In order to arrest any sodium sulphate which might be carried as fine spray along with the stream of gas, the latter is made to bubble through a strong solution of hydrochloric acid contained in a three-necked bottle, B, before being passed into the brine. The tube which delivers the gas into the salt solution should be sufficiently wide not to become stopped up with the deposited salt, and need

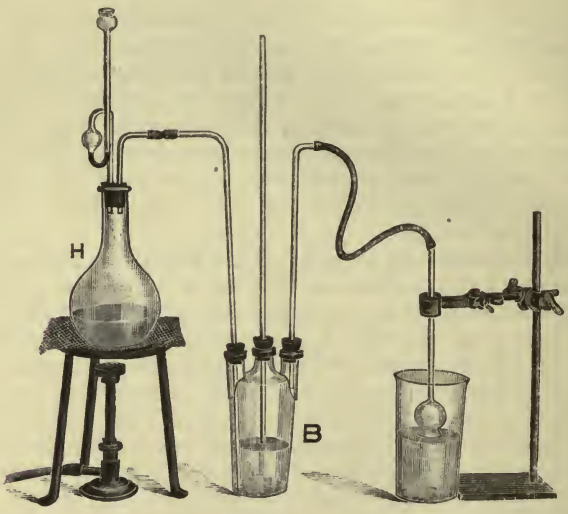

FIG. 36.

not dip very far into the solution. An ordinary thistle funnel, supported as shown in the figure, is convenient.

The generating flask should be provided with a safety funnel, and the wash-bottle B with a tube which just dips beneath the surface of the liquid. In this way, should there be any interruption in the evolution of gas, there is no possibility of the brine being sucked back into B, as, directly a reduction of pressure takes place within the apparatus, air is drawn in through the safety tubes.

As the gas begins to bubble into the brine, the salt almost immediately commences to separate out as a crystalline powder.

When a sufficient quantity of the salt has been precipitated, the crystals are allowed to settle, and the bulk of the liquid decanted off. The salt is then thrown upon a drainer (which may be connected to a water-pump, as on p. 212), and after as much as possible of the mother-liquor has drained away, the salt is rinsed two or three times with a little strong hydrochloric acid (pure). It is then removed to a porous plate to dry, after which it is heated in a porcelain evaporating-dish, by means of a "rose" burner, until all traces of water and hydrochloric acid are expelled.

(2) *Precipitation of ferrous sulphate*, $FeSO_4,7H_2O$, *by alcohol.*—A convenient quantity of ferrous sulphate (say 100 grams) is dissolved in water at a temperature of about 40° C. The salt should be placed in a beaker, and a quantity of water having a temperature of about 40° added to it. The temperature of the mixture at once falls, perhaps as much as 10°, owing to the absorption of heat due to solution. The beaker is then placed in a larger beaker or other vessel containing water at 40°, and the solution constantly stirred until the whole of the salt has dissolved and a tolerably saturated solution obtained at that temperature. The solution is acidified with two or three drops of dilute sulphuric acid, and then filtered. To prevent oxidation by undue exposure to the air, the filtering operation should be accelerated by means of the filter-pump* (p. 212). The perfectly clear greenish solution thus obtained

* As ordinary filter-paper, when wet, is not strong enough, when folded and used in the ordinary way, to stand the pressure to which it would be exposed by the use of the filter-pump, special devices must be employed for its support.

One method most suitable for such occasions as that under consideration, where great rapidity is an advantage, is to place in the funnel a porcelain drainer, and to lay upon it a small circular disc of ordinary filter-paper cut a trifle larger (about 2 mm. all round) than the drainer. The paper is moistened and carefully adjusted so as to entirely cover the drainer. [In some cases where a very high degree of exhaustion is necessary, a circular piece of muslin or thin calico should be laid under the paper.]

Where the filter-pump is used for precipitates that are afterwards to be dried and weighed, as in the usual quantitative determinations, one of the two following plans is usually adopted: Either a specially prepared toughened paper is used (Schleicher and Schüll, No. 575), or the ordinary paper is supported at the apex of the cone by means of a small muslin or a platinum cone. When muslin is used, a small circular piece (conveniently cut to the size of a penny piece) is folded as a filter is folded, and placed in the funnel. The folded filter-paper is then introduced, being carefully pushed into its position with its apex within the muslin cone. The filter-paper *must* fit the funnel

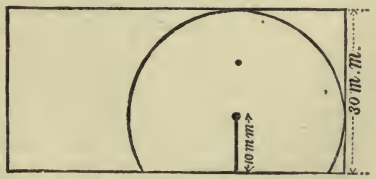

FIG. 37.

is poured into a quantity of alcohol (methylated spirit) about equal to the volume of the ferrous sulphate solution. The first effect will be somewhat unexpected, for, instead of any precipitation of crystals, a green liquid separates out at the bottom of the vessel. On stirring the mixture, however, for a moment or two, this liquid disappears, and the ferrous sulphate is precipitated as a fine crystalline powder. The liquor is then decanted off, the crystals drained upon a drainer and rinsed with alcohol. It must then be dried as quickly as possible upon a porous plate, or by gentle pressure between folds of blotting-paper.

Precipitation by Double Decomposition.—The process of preparing a pure compound by this method is practically identical with that of conducting any quantitative precipitation. It will be obvious that, in order to obtain a pure product, there must be nothing present which will give a precipitate with the reagent to be used, other than the compound intended. For instance, suppose it is desired to prepare pure barium carbonate by precipitation from a solution of barium chloride by means of ammonium carbonate; the barium chloride must itself be a purified salt, and must be free from any metallic compounds which would give a precipitate with ammonium carbonate. The precipitated compound is washed with warm water until perfectly free from any soluble salts, and is finally dried in a steam-oven if it can stand that temperature without decomposition, otherwise it is spread upon a porous plate.

When it is desired to crystallise a salt with the object of obtaining large and well-defined crystals, it is necessary to modify the methods so as to cause the process to take place very slowly, and, as nearly as possible, with uniform regularity. A nearly saturated solution of the salt is made at a temperature about 30° C., using a considerable volume of water. The solution is placed in a beaker, which is then stood in a larger beaker of warm water in order to render the cooling operation slower, and covered with a clock-glass. When the solution is cold, there will be a small crop of

exactly, and not leave any air-spaces down the sides. If the sides of the funnel do not enclose an angle of exactly 60°, the paper must be folded so as to make it exactly fit the funnel, or the funnel must be rejected for one of the right shape. A platinum cone is made by cutting from a piece of foil a segment of a circle whose radius is 15 mm. (or $\frac{3}{4}$ inch). The segment should be nearly three-quarters of the entire circle, as shown in Fig. 37, so that when it is bent together so as to form the cone, there will be an overlap extending almost one-half of the way round. A few fine holes may be pierced in the metal near to the apex of the cone, by laying the flat piece of foil upon a cork, and pricking it with a fine needle. The cone is then put into the funnel with the paper just as the muslin cone. Sometimes a cone of the toughened paper above mentioned is used; this is less advantageous, as it practically introduces a double filtering medium, and retards the process considerably.

crystals on the bottom of the beaker. The liquid is then poured into another beaker, and a few of the best formed of the crystals are picked out. (If this first crystallisation has resulted in the deposition of a solid cake or crust, and no isolated crystals, the liquid must be returned to the beaker, and the whole warmed up again, with the addition of a little more water, and the solution set to cool as before.) These are dropped into the cold mother-liquor so as to lie isolated from each other, and the vessel placed where its temperature will remain as nearly constant as possible. The rate of evaporation of the liquid may be checked, if the salt deposits too quickly, by partially covering the beaker. If circumstances make it necessary that the operation be carried on in a room liable to considerable changes of temperature, it is a good plan to keep the beaker in a larger vessel of water all the time the process is going on. In order that the crystals may become equally developed in every direction, so as to approach as nearly as possible the perfect form for the particular compound being crystallised, they must be turned at regular intervals, say every day, or every second day, according to the rate of growth, so as to rest upon a different face. The more slowly the crystals can be grown, other things being equal, the more perfect in form will they be.

In cases where the solution cannot be left exposed to the air for so long without undergoing some chemical change (for instance, ferrous sulphate would become oxidised), the salt may be slowly crystallised, if it is one which is insoluble in alcohol, by allowing that liquid to very gradually diffuse into the aqueous solution. To take the case of ferrous sulphate as an example. A strong cold aqueous solution of the salt is placed in a large wide-mouth stoppered bottle, which is less than half filled by it. A layer of water about $2\frac{1}{2}$ c.c. (1 inch) deep is floated upon the top of the solution, and upon the top of the water a quantity of alcohol is placed, equal to the volume of liquid already present. The stopper is inserted, and the bottle placed where it can remain for some weeks undisturbed. By slow degrees the alcohol diffuses into the aqueous solution, and thereby causes the gradual deposition of crystals of the salt.

The object of the shallow layer of water dividing the alcohol from the saline solution is to prevent the precipitation of the salt at the surface of contact, which would be the case if the alcohol floated immediately upon the solution.

A good plan for floating one liquid upon another without causing admixture, is the following :—

The heaviest solution is first poured into the vessel by means of a funnel with a long stem, so as not to splash the sides of the vessel. A thin circular disc of cork, as large as will pass the mouth of the bottle, is then lowered on to the surface of the solution by means of a fine thread attached to the centre of the cork with a little wire hook.

By means of a stoppered funnel, attached to a long piece of

glass tube drawn to a narrow jet at the lower end, the lighter liquid (in the above instance, the *water*) is allowed slowly to stream on to the cork, the funnel being gradually raised as the cork ascends, so as to keep the jet almost close to the latter, as shown in Fig. 38.

When a sufficient layer of the second liquid has been floated upon the first, the still less dense third liquid (the *alcohol* in the

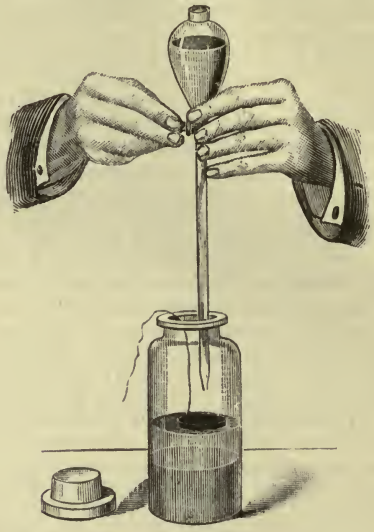

FIG. 38.

example) is introduced in the same way. As the layer of the added liquid gradually gets deeper, and the cork float is further removed from the line of contact, the liquid may be run in more quickly, without fear of disturbing the solution below. When all has been added, the cork is withdrawn by means of the thread, and the bottle stoppered. (The cork should be put into hot water to soak, if it is intended to use it again for a similar purpose.)

SECTION II.

Typical Gravimetric Estimations of Metals.

In order to make a gravimetric estimation of a metal, the latter is either obtained from the compound in the elemental form, and the metal itself weighed; or it is caused to enter into some convenient combination, yielding a compound of known and definite composition, and from the weight of the compound so produced the quantity of metal is ascertained by calculation. This latter mode is of more general application than the first, as many of the metals are not easily reduced from their compounds. Of late years, however, electrolytic methods of analysis have been greatly developed and perfected, so that a large number of metals, which formerly could only be determined in combination, are now deposited in the form of metal, and so weighed. Typical examples of this process of analysis will be given in a separate section.

The forms of combination which are most frequently had recourse to, and which are applicable to various metals, are practically three in number, namely, the *oxide*, *sulphide*, and *sulphate*.

When weighed in the form of an oxide, the metal is first precipitated either as a *hydroxide* (as, for example, in the case of Al, Fe, Cr, Ni, Cu, etc.) or as a *carbonate* (as in the case of Bi, Mn, Zn, etc.). In either case the precipitated compound is converted by heat into the oxide, which is then weighed.

When estimated as a sulphide, the metal is precipitated in this form of combination either by sulphuretted hydrogen or ammonium sulphide. Examples of metals which may be estimated in this way are seen in *mercury*, *cadmium*, *antimony*, and *arsenic*. Metals which are to be weighed as sulphates, are either precipitated from solution in this form, as in the case of *lead*, *barium*, and *strontium*, or the sulphate is obtained by evaporating a suitable compound of the metal (*e.g.* the chloride) with sulphuric acid, whereby it becomes converted into the sulphate. This method is sometimes employed for the estimation of the alkali metals.

Besides these methods, each of which is applicable for the estimation of *several* metals, there are special forms of combination which are available for special cases. Thus, for example, silver is precipitated and weighed as chloride (or bromide); magnesium is precipitated as ammonium magnesium phosphate, which is then converted into magnesium pyrophosphate by the action of heat, and weighed in this form; and so on.

Descriptions will be given in this section of a selected number of typical examples, illustrating the most important methods of gravimetric estimations, and forming a suitable course for practice in the various analytical operations.

Estimation of Aluminium.

Epitome of Process.—The metal is precipitated from the solution of its compounds as aluminium hydroxide by means of ammonia.* The hydroxide is afterwards converted by heat into the oxide, Al_2O_3, in which form the metal is weighed.

Employ potassium alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, taking about 2 grams.†

A stoppered weighing-bottle containing powdered alum, which has been purified by re-crystallisation, is first weighed; after which about 2 grams of the salt are carefully transferred without loss to a beaker,‡ conveniently of about 550 c.c. (nearly 20 ozs.) capacity. (The stopper should be removed from the bottle while the latter is held immediately over the beaker. A sufficient quantity of the salt is then tipped out and the stopper again replaced, care being taken that no particles are left adhering to the lip of the bottle, by giving the latter a few taps with the finger.) The beaker is

* The precipitation of metallic hydroxides by alkalies is not complete in the presence of certain organic substances, such as tartaric or citric acids, sugar, etc. In cases where such non-volatile organic matter is present, these must first be decomposed by adding to the solution sodium carbonate and potassium nitrate, and evaporating to dryness in a platinum dish, upon a steam-bath. The residue is then fused, and afterwards extracted with dilute hydrochloric acid. The solution is then filtered, and the precipitation conducted as above described.

† See note on p. 201. In this case, the formula weight of alum being 948, while that of Al_2O_3 is only 102, the final product that is to be weighed amounts to less than one-ninth of the weight of the original salt. Hence a fair quantity must be operated upon. Two grams of the salt will only furnish about 0·21 grams of Al_2O_3. When estimating the (SO_4) in alum the case is different, for the weight of the $BaSO_4$ yielded is nearly equal to the original weight of the alum itself.

‡ In special cases, where exceptional accuracy is required, a vessel of platinum, nickel, or porcelain is substituted for the beaker, as alkalies exert a slight solvent action upon the glass. With Jena glass this action is extremely slight.

immediately covered with a clock-glass. The bottle is then weighed again, and the difference gives the weight of alum taken.

The salt is then dissolved in such a quantity of water that the beaker is about one-fourth part filled with liquid,* and the process of solution is aided by gently warming the mixture.

For this purpose the beaker may be supported and heated by either of the methods shown on p. 209, Figs. 30 and 31; or it may be placed upon an iron plate heated by a Bunsen, as in Fig. 39.

Fig. 39.

This is a specially convenient arrangement when several operations are being conducted simultaneously. The heat can be moderated by placing the vessel nearer to, or farther from the flame. A piece of asbestos cloth laid upon the top of the plate prevents any risk of the fracture of glass vessels by placing them suddenly upon the rough iron. It is important that the various pieces of apparatus used should bear a suitable relation to each other as regards their size. For example, the clock-glass employed as a cover should not be much larger than the mouth of the beaker; and when a flame is used directly under the vessel, care must be taken that it does not extend beyond the bottom of the beaker. Such an arrangement

* In all the following examples, the size of the beaker, and the quantity of water employed for the solution of the salt, may be the same as those here described, unless special directions to the contrary are given. It ought not to be necessary to repeat at this stage, what was stated on pp. 3 and 116, that in all analytical operations *distilled* water must be exclusively used.

of apparatus as shown in Fig. 40, and which is not unfrequently seen in the laboratory, is almost sure to end in disaster. The heat from the lamp either fractures the clock-glass, fragments of which fall into the solution, or the beaker itself becomes unduly heated upon its sides, so that the first movement of the liquid causes it to crack. The beaker should be kept covered by the clock-glass as much as possible throughout the entire operation.

Fig. 40.

A quantity of ammonium chloride solution is added,* equal to about a fourth of the volume of the liquid already present, and then ammonia in the least possible excess beyond that which is required for complete precipitation.

The mixture is stirred with a glass rod with rounded ends, the rod being of such a length that it will just stand in the beaker while the cover is upon it. A short piece of clean narrow caoutchouc tube should be previously fitted upon the end of the rod. This not only prevents the beaker from becoming scratched by the rod, but it is useful in the subsequent operation of removing particles of the precipitate which may adhere to the sides of the beaker.

The liquid is then boiled until the greater part of the ammonia is expelled, and the issuing steam possesses only a slight smell of the reagent.

The precipitate is then allowed to settle ; the clock-glass is removed, and the under side rinsed into the beaker by means of a fine jet of hot water from a wash-bottle, in case any particles may have been thrown up during the operation of boiling. The clear liquid is then decanted off through a filter,† the weight of whose ash is known (see p. 206).

When as much of the liquid as possible has been poured off

* In the presence of ammonium chloride, aluminium hydroxide is insoluble in ammonia.

† The operation of filtering must be carried out with all the precautions against loss described in the introduction to qualitative analysis, p. 2. It sometimes happens, owing to the particular shape of the lip of a beaker, that, even when the liquid is carefully poured down against a glass rod, a little of it creeps back under the edge. This may be prevented by slightly greasing the under side of the lip by means of a little touch of vaseline or resin cerate upon the finger.

without disturbing the precipitate, the beaker is half filled up with boiling water, the mixture well stirred, and, after being allowed to settle, is decanted as before through the same filter. This process is repeated a second time, after which the precipitate itself is transferred to the filter. Every trace is removed from the sides of the beaker by the aid of the glass rod, and the beaker is finally rinsed into the funnel by means of a jet of hot water from the wash-bottle in the manner shown in Fig. 41, the movable nozzle of the bottle being directed round the beaker by the fore-finger.

The final washing of the precipitate is now made upon the filter by means of the jet of hot water from the wash-bottle, washing downwards from the upper edge of the paper, but never quite filling the paper cone with water, and allowing each washing to drain completely through before adding fresh water.* The operation is continued until the precipitate is entirely freed from all soluble salts, which in this case consist of sulphates of potassium and ammonium. To ascertain when this is the case, a few drops of the filtrate are collected in a test-tube, and a little barium chloride added. If no precipitate forms in a few minutes after warming the mixture, the washing may be considered complete. The last washing should aim at collecting the precipitate together into the cone of the filter.

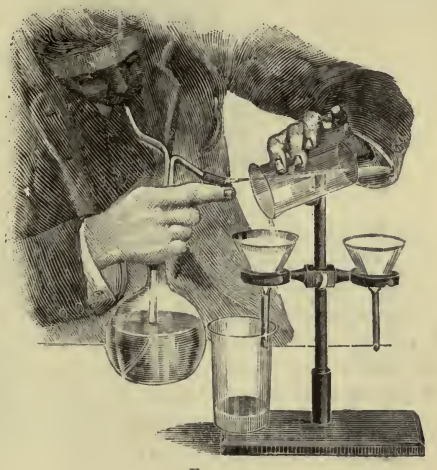

Fig. 41.

The filter and precipitate are next dried in a steam-oven. For this purpose, the funnel containing the filter is covered with a piece

* When a filter-pump is being used, however, this rule does not apply. In this case it is important *not* to let the filter run empty, but to constantly add liquid before the former quantity has completely run through, otherwise channels or fissures are liable to be formed in the solid material upon the filter through which subsequent wash-waters run without properly washing the precipitate.

of filter-paper, and either stood up in the corner of the oven, or placed in a conical tin support. In order to securely cover the funnel, a common circular filter-paper, somewhat larger in diameter than the top of the funnel, is held upon the latter with the left hand, while the projecting paper is folded down all round with the other hand in the manner shown in Fig. 42.

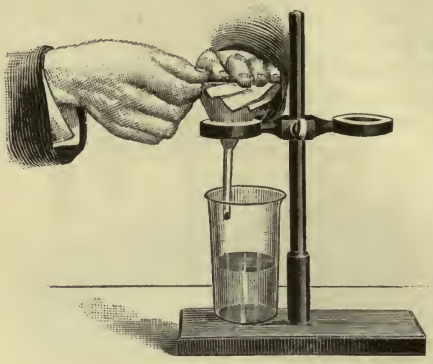

FIG. 42.

While the precipitate is drying, a platinum crucible is heated to redness for a few moments, cooled in the desiccator, and then weighed. The dried filter containing the aluminium hydroxide is then removed from the funnel, carefully folded up, and placed in the weighed crucible. The crucible, supported upon a clean pipeclay triangle, is first very gently heated, the lid being placed slightly on one side in order to allow the gaseous products of the combustion of the paper to escape, and also to admit the necessary supply of air for the combustion. When the active combustion of the paper has subsided, the temperature is gradually raised, and when it has reached a red heat, the lid of the crucible may be removed.* The vessel is maintained at a bright

* It is very necessary that the tips of the crucible-tongs should be perfectly

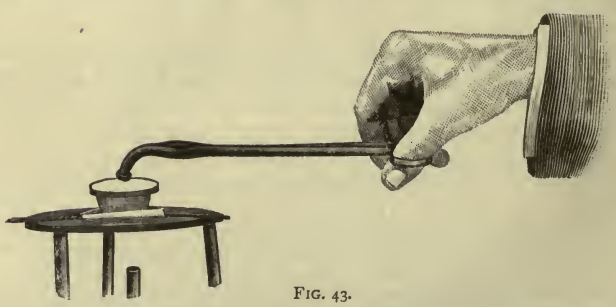

FIG. 43.

clean, and after being in contact with the hot crucible or lid, the tongs should *never be placed on the table with the tips downward.* The first impulse of almost

red heat by means of a good Bunsen flame or a blowpipe for about ten minutes. The lid is then replaced, and the crucible

every one is to hold and use crucible-tongs in the manner shown in Fig. 43, with the almost inevitable result that when putting them down, the hot points

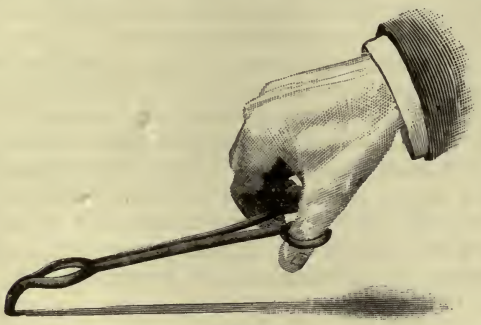

FIG. 44.

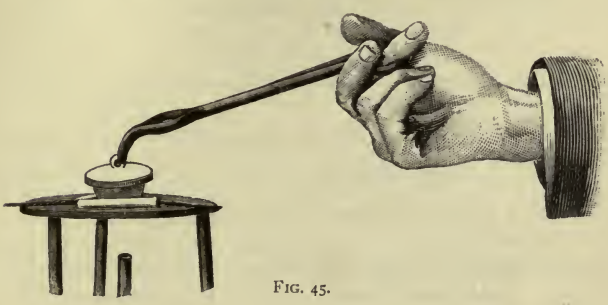

FIG. 45.

come into contact with the wooden table (Fig. 44), and are liable to pick up matter which afterwards may be transferred to the crucible. Tongs should always be held in exactly the reverse way, with the tips pointing in the direction of the *back* of the hand, as in Fig. 45. They are then naturally placed upon the table with the tips pointing upwards (Fig. 46). The habit of manipulating tongs in this way should be cultivated from the very beginning.

FIG. 46.

transferred to the desiccator to cool, after which it is weighed. It is reheated for a similar time and again weighed, the operation being repeated until the weight is practically constant.

[When a filter-pump is employed for accelerating the filtration of the aluminium hydroxide, the precipitate may be partially dried by allowing the pump to continue in operation for fifteen minutes or so after all the liquid has passed through. The filter may then be folded up, and at once transferred to the crucible, in which it is completely dried by the cautious application of heat. To avoid *spitting*, the crucible should be supported rather obliquely in the triangle, and a small flame applied to the extreme upper part, so that the heat may be conducted very gently to the wet materials.]

From the data obtained by the analysis, the percentage of aluminium is calculated in the following manner :—

Estimation of Aluminium in Potash Alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$.—

Weighing-bottle and salt (first weight)		16·9485 grams.
,, ,, ,, (second weight)		14·8870 ,,
Weight of salt taken		2·0615 ,,
Weight of crucible + filter-ash + Al_2O_3		25·6857
Weight of crucible alone	25·4635	
Weight of ash *	0·0002	
		25·4637
Weight of Al_2O_3		0·2220

$$\left.\begin{array}{l}\text{Formula-weight of } Al_2O_3 = 102\\ \text{,, ,, } Al_2 = 54\\ \text{therefore weight of aluminium in 0·2220 gram } Al_2O_3\dagger\end{array}\right\} = \frac{54 \times 0{\cdot}2220}{102} = 0{\cdot}11753$$

$$\text{hence the percentage of aluminium found} = \frac{0{\cdot}11753 \times 100}{2{\cdot}0615} = 5{\cdot}70$$

* If the filter employed is that mentioned on p. 193, having an ash equal to 0·00017, it may be ignored altogether, as it does not affect the second place of decimals in the final result.

† The ratio 102 : 54 is equal to 1 : 0·5294, therefore the weight of Al in any given weight of Al_2O_3 is at once obtained by multiplying the latter by the factor 0·5294. Thus, in the above example, $0{\cdot}2220 \times 0{\cdot}5294 = 0{\cdot}117526$. At the commencement of each estimation in this section, the factor will be found, which, when multiplied by the weight of the compound that is actually weighed, will give the weight of metal it contains. The use of *factors*, especially by the student, is always attended with the danger of obscuring the *rationale* of the calculation, and reducing it to a mechanical or "rule of thumb" operation. To prevent this as far as possible, the ratio of the formula-weights of the compound weighed, and the metal to be estimated are given, so as to keep present to the mind the true significance of the factor.

$$\left\{\begin{array}{l}\text{Formula-weight of } K_2SO_4,Al_2(SO_4)_3,24H_2O = 948\\ \text{Formula-weight of } Al_2 = 54\\ \text{hence the theoretical percentage of aluminium in alum}\end{array}\right\} = \frac{54 \times 100}{948} = 5{\cdot}69$$

Chromium.

Epitome of Process.—The chromium is precipitated from solutions of *chromic* compounds in the form of chromic hydroxide by means of ammonia. The hydroxide is converted by heat into chromic oxide, Cr_2O_3, in which form the element is weighed.

Chromates are first reduced to the "chromic" state by means of sulphur dioxide. Factor—

$$(Cr_2O_3)\ 152 : (Cr_2)\ 104 = 1 : 0{\cdot}68421$$

Estimation of Chromium in Chrome Alum, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$.—Employ about 1·5 gram. The process is conducted exactly as in the case of aluminium, except that the addition of ammonium chloride may be omitted. The filter may either be burnt in the crucible along with the precipitate, or it may be incinerated separately, as described below in the case of iron. Chromium oxide is not reduced during the process.

Formula weight of chrome alum = 998. Theoretical percentage of Cr = 10·42.

Estimation of Chromium in Potassium Dichromate, $K_2Cr_2O_7$.—Take about 0·75 gram. The purified salt is weighed out into a beaker (see notes, pp. 222, 223), and dissolved in water without being warmed. A gentle stream of sulphur dioxide * is passed through the liquid until the chromium is wholly reduced to the "chromic" state. The reduction is complete when the solution, on being gently moved against the sides of the beaker, shows no trace of the yellow colour, but has a clear green tint. The delivery tube is rinsed into the beaker with water from the wash-bottle, and removed. The solution is then warmed to expel the excess of sulphurous acid, and is afterwards precipitated with ammonia as in the above example.

Formula-weight of potassium dichromate = 294. Theoretical percentage of Cr = 35·37.

* The sulphur dioxide is most conveniently derived from a "syphon" of the liquefied gas. In the absence of such a supply, the gas must be generated from sulphuric acid and copper. In this case the sulphur dioxide must be washed by being passed through water before being delivered into the solution of the chromate.

Iron.

Epitome of Process.—The iron is precipitated from solutions of *ferric* compounds as ferric hydroxide by means of ammonia. The hydroxide is converted by heat into ferric oxide, Fe_2O_3, in which form the metal is weighed. The filter is burnt apart from the precipitate. The iron in *ferrous* compounds is first oxidised into the "ferric" state. Factor—

$$(Fe_2O_3)\ 160 : (Fe_2)\ 112 = 1 : 0{\cdot}700$$

Estimation of Iron in Ferrous Ammonium Sulphate, $(NH_4)_2SO_4,FeSO_4,6H_2O$.—Employ about 1·5 gram. The purified salt is weighed out into a beaker (notes, pp. 222, 223), and dissolved in water with the addition of one or two drops of dilute sulphuric acid. The solution is warmed, and a little strong nitric acid added, sufficient to oxidise the whole of the iron. The mixture is heated nearly to the boiling-point for a short time in a covered beaker. Each drop of nitric acid as it is added produces a brown coloration, owing to the absorption of the disengaged nitric oxide by the ferrous salt; but when the oxidation is complete, the addition of a drop of the acid produces no visible effect. By adding, therefore, a few drops of nitric acid after its addition has ceased to cause any coloration, sufficient will have been introduced to complete the oxidation. As a confirmation, the smallest drop of the solution is placed upon a piece of white porcelain (such as a crucible lid) by means of a glass rod, and the drop is touched with *another* glass rod which has been dipped in a solution of potassium ferricyanide. If the ferrous iron has been completely oxidised, no blue coloration will result. [The ferricyanide solution must be *freshly* made, by dissolving a small crystal of the salt in water.]

The ferric hydroxide is then precipitated by the addition of a slight excess of ammonia, and the mixture boiled until the steam scarcely smells of ammonia. The precipitate is washed with hot water by decantation two or three times, and finally washed upon the filter until the wash-water is entirely free from sulphates (compare Aluminium, p. 225).

The precipitate is then thoroughly dried in the steam-oven.

When perfectly dry, the filter is withdrawn from the funnel, and as much of the precipitate as possible is detached from the paper by gently squeezing the cone together, and transferred to a platinum crucible, which is placed upon a sheet of glazed paper (see p. 207). By flattening the paper cone and gently rubbing one side against the other, the remaining adhering particles may be detached. The paper is then folded in the manner described on p. 207, bound up

in a platinum wire, and incinerated as completely as possible. The ash is then shaken off the wire into the crucible, and any particles which may have fallen upon the glazed paper are also carefully swept into the crucible by means of a feather. The crucible is then heated for about ten minutes to a bright red heat by means of a Bunsen flame, after which it is placed to cool in the desiccator and weighed; the heating and weighing being repeated until no further loss of weight results.

The minute quantity of ferric oxide which is left upon the filter, and which becomes reduced to metallic iron during incineration, is again oxidised during the process of heating; and, although it may not pass into the same oxide, Fe_2O_3, but probably into Fe_3O_4, the total quantity is so small, and the ratio $Fe_3O_4 : (Fe_3)$ is so nearly equal to $Fe_2O_3 : (Fe_2)$, that the difference is quite outside the experimental error.

Formula weight of $(NH_4)_2SO_4,FeSO_4,6H_2O = 392$. Theoretical percentage of Fe = 14·28.

Calcium.

Epitome of Process.—The calcium is precipitated in the form of calcium oxalate, CaC_2O_4, by means of ammonium oxalate in the presence of ammonia. The calcium oxalate is then converted by a *gentle* heat into calcium carbonate, $CaCO_3$, in which form the metal is weighed; or it is *strongly* heated until it is entirely changed into calcium oxide, and weighed in this form.

As an exercise in manipulation, the oxalate may be converted first into the carbonate and weighed, and afterwards, by the application of a stronger heat, be changed into the oxide and weighed again. Factors—

$$(CaCO_3)\ 100 : (Ca)\ 40 = 1 : 0{\cdot}4000$$
$$(CaO)\ 56 : (Ca)\ 40 = 1 : 0{\cdot}71428$$

Estimation of Calcium in Calcium Carbonate, $CaCO_3$.—Employ about 0·5 to 0·75 gram. Pure precipitated calcium carbonate is weighed out into a beaker, and dissolved in a very little dilute hydrochloric acid. The clock-glass cover should be pushed a little to one side, and the diluted acid poured gradually down the side of the beaker. When the carbonate is completely dissolved, the cover should be rinsed into the beaker by means of the wash-bottle, and water added until about the usual volume is present. Ammonia is then added until the solution smells distinctly of the reagent, and the liquid is heated to boiling. The calcium oxalate is then precipitated by the addition of a slight excess of a warm strong solution of ammonium oxalate, to which a little ammonia has been added.

The mixture is boiled for a few minutes, and allowed to settle.* The clear liquid is then decanted off through a filter, without disturbing the precipitate. It is washed three or four times by decantation with boiling water, allowing it to settle thoroughly each time. The small quantity of the precipitate which is inevitably conveyed to the filter with the washings, will so far fill up the pores of the paper that, when, after the third or fourth wash, the precipitate itself is transferred to the filter, the filtrate will be perfectly clear. The precipitate is washed with warm water until the wash-water is free from ammonium chloride, as indicated by the absence of any milkiness on the addition of silver nitrate after acidifying with nitric acid.

When washing this precipitate, a fine jet of water should be employed, and it should be made to impinge *first* upon the glass funnel above the edge of the paper, and then gradually directed down towards the precipitate.

After being dried in the steam-oven, the precipitate is transferred as completely as possible to a platinum crucible. The filter is incinerated in a platinum wire coil, and the ash deposited in the crucible. The calcium oxalate is then converted by a gentle heat into the carbonate, the temperature being carefully regulated so that it never reaches a visible redness even at the bottom of the crucible. A convenient plan, in order to avoid unduly heating any spot of the crucible, is to place it upon a triangle arranged above a piece of wire gauze upon a tripod, as shown in Fig. 47. The gauze is heated to redness by means of a rose burner, the heat being thus radiated to the crucible, which must be heated in this manner for

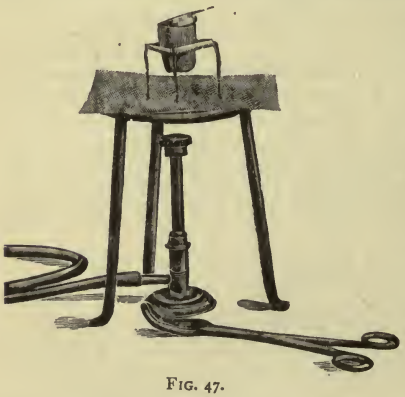

FIG. 47.

* Calcium oxalate is a precipitate requiring some special care in its manipulation. Under ordinary circumstances it is somewhat slow to settle, showing an inclination to creep up the wet sides of the beaker, and it also passes through the filter very easily. By conducting the precipitation in the manner here described, the compound is obtained in a more coherent form, and with a little care will be perfectly retained by the filter.

about fifteen minutes; it is then cooled in the desiccator and weighed.

In case any of the calcium carbonate has become converted into the oxide in spite of care in the heating, the residue is moistened with a few drops of a strong solution of ammonium carbonate, which is then evaporated to dryness by placing the crucible in the steam-oven. When dry, it is reheated *for a few minutes* over the heated gauze, and again weighed.

If this process results in any increase in the weight, it shows that in the first heating some of the carbonate had been decomposed; the series of operations should, therefore, be repeated until the weight remains constant.

In this particular instance the form of combination in which the metal to be estimated is weighed, happens to be the same as that in which it exists in the original compound, namely, the *carbonate;* hence the weight of the product obtained will be the same as that of the substance taken for analysis.

The calcium carbonate is now converted entirely into calcium oxide by heating the crucible to a strong red heat by means of a Bunsen flame for about ten minutes, and finishing off with a blowpipe flame. The crucible is placed in the desiccator to cool, and is then weighed. It is afterwards reheated with the blowpipe for a few minutes and weighed again, the process being repeated until no further loss of weight results.

Magnesium.

Epitome of Process.—The magnesium is precipitated by sodium phosphate, in the presence of ammonium chloride and ammonia, as ammonium magnesium phosphate, $NH_4MgPO_4,6H_2O$. This is afterwards converted by heat into magnesium pyrophosphate, $Mg_2P_2O_7$, in which form the metal is weighed. Factor—

$$(Mg_2P_2O_7)\ 222 : (Mg_2)\ 48 = 1 : 0{\cdot}2162$$

Estimation of Magnesium in Magnesium Sulphate, $MgSO_4,7H_2O$.—Take about ·75 gram. The recrystallised salt is weighed out into a beaker, and dissolved in a rather smaller bulk of water than usual (about 60 to 80 c.c.). A quantity of ammonium chloride solution is added, equal to about one-half the volume of the solution of magnesium sulphate, and then ammonia in moderate excess.* To this is added a solution of hydrogen disodium

* Should the addition of ammonia cause precipitation, more ammonium chloride must be introduced until this precipitate is redissolved. Excess of ammonia, over and above that which is required for the formation of the ammonium magnesium phosphate, is necessary to ensure complete precipitation, as the phosphate is slightly soluble in water, but insoluble in the presence of free ammonia.

phosphate, in quantity in excess of that required for complete precipitation of the ammonium magnesium phosphate. The mixture must be well stirred with a rubber-tipped glass rod. The precipitate is a crystalline compound, which requires several hours for its complete separation. Its formation is accelerated by stirring or shaking, but care is necessary to avoid pressing or rubbing the *glass* of the stirring-rod against the sides of the beaker, as this would cause the deposition of minute crystals upon the surface of the vessel, which are very difficult to detach. The covered beaker should be put aside for a few hours.*

The liquid is filtered, and the precipitate washed with dilute ammonia (water 3 parts by volume, strong ammonia sp. gr. ·880 1 part) until the filtrate is perfectly free from chloride, as indicated by the absence of any milkiness when tested with silver nitrate after acidification with nitric acid.

The precipitate is then dried in the steam-oven.

The dry precipitate is transferred to a platinum crucible, and the filter incinerated in a platinum coil. Care should be taken not to overheat the filter during this operation, whereby the adhering precipitate becomes fused, and thereby renders the complete combustion of the paper extremely difficult.† After the ash has been placed in the crucible, the latter is gently heated by means of a small Bunsen flame. The crucible must be covered during this operation, and the heat must be applied cautiously, as, during the conversion of the compound into the pyrophosphate, ammonia and water are eliminated, and, in escaping too rapidly, these would cause loss of the precipitate. When the smell of ammonia can no longer be perceived, the temperature is gradually raised to a bright red heat, finishing off with a blowpipe flame.

The crucible is then removed to the desiccator to cool, and afterwards weighed, the heating process being repeated until the weight is constant.

Formula weight of $MgSO_4,7H_2O = 246$. Theoretical percentage of Mg = 9·756.

* If the entire operation be carried out in a 500 c.c. wide-mouth stoppered bottle, and the mixture be briskly shaken for a few minutes, the precipitation will be complete in a very short time. The disadvantage of this plan is the greater difficulty of transferring the precipitate to the filter. When the stopper is removed, it must be carefully rinsed with water.

† The incineration may be made by the alternative method described for magnesium arsenate, p. 254.

Copper.

I. As Copper Oxide.

Epitome of Process.*—The copper is precipitated from solutions of its salts in the form of copper hydroxide by means of potassium hydroxide. The copper hydroxide is subsequently converted by heat into copper oxide, in which form the metal is weighed. The filter is burnt apart from the oxide, and treated in a special manner. Factor—

$$(CuO)\ 79{\cdot}3 : (Cu)\ 63{\cdot}3 = 1 : 0{\cdot}79823$$

Estimation of Copper in Copper Sulphate, $CuSO_4,5H_2O$. —Employ about 1 gram. The recrystallised salt is weighed out into a beaker,† and dissolved in water with the aid of heat. The solution is raised to the boiling-point, and potassium hydroxide added in small quantities with constant stirring, until precipitation is complete. When this is the case, the liquid will appear colourless as the precipitate settles, and a drop of the clear liquid placed on turmeric paper by means of a glass rod, will show that the solution is alkaline.

The mixture is gently boiled for a few minutes, and then allowed to settle.

The precipitate is washed two or three times by decantation with boiling water, and then transferred to the filter, when the washing is continued with hot water from the wash-bottle until the filtrate is perfectly free from potassium sulphate, as indicated by barium chloride. The funnel is then covered, and placed to dry in the steam-oven.

The dried precipitate is transferred to a platinum crucible, and as much as possible of that which adheres to the paper is detached by the process of gently rubbing the sides of the filter together.

The paper is folded up for incineration, so that that portion which is soiled with the precipitate shall be in the interior of the roll, and shall not come in contact with the platinum wire.

By giving the crucible a gentle tap, the precipitate is made to take up a position rather to one side, and so leave a clear space, upon which the ash may be deposited.

After the ash has been dropped into the crucible, a single drop

* See note *, p. 222, with reference to the presence of organic matter. In the case of copper hydroxide, precipitation is also incomplete if much alkali nitrate is present. In such cases the copper may be estimated as sulphide (p. 236).

† See note ‡, p. 222, which applies still more in the case of caustic potash or soda.

of strong nitric acid is allowed to fall upon it from a pipette. Any particles of reduced copper are thus converted into the nitrate, which, in the subsequent heating operation is decomposed, leaving copper oxide.

The crucible is first gently warmed to expel the excess of nitric acid, after which it is raised to a red heat, and maintained at this temperature for about ten minutes. It is then allowed to cool in the desiccator, and weighed. The heating is repeated until the weight is practically constant.

Formula weight of $CuSO_4.5H_2O = 249{\cdot}3$. Theoretical percentage of Cu = 25·35.

II. As Copper Sulphide.

Epitome of Process. — The copper is precipitated from neutral or acid solutions as cupric sulphide, CuS, by means of sulphuretted hydrogen. The cupric sulphide is then converted by heat into cuprous sulphide, Cu_2S, in which form the metal is weighed. Factor—

$$(Cu_2S)\ 158{\cdot}6 : (Cu_2)\ 126{\cdot}6 = 1 : 0{\cdot}79823$$

Estimation of Copper in Copper Sulphate, $CuSO_4,5H_2O$. —Take about 1 gram. The weighed-out salt is dissolved in hot water, in quantity sufficient to about half fill the beaker, and a few cubic centimetres of strong hydrochloric acid are added. A stream of sulphuretted hydrogen is then passed through the solution, until precipitation is complete.

The precipitate is at once filtered, the funnel being covered with a clock-glass to prevent atmospheric oxidation of the copper sulphide into *sulphate*, which would pass into solution and be lost.* The filter should be continuously replenished, and not allowed to run dry. The precipitate is washed down into the apex of the filter with warm sulphuretted hydrogen water, and as in this instance the solution contains no soluble salts, two or three rinses with the warm sulphuretted hydrogen water will be sufficient to wash out the acid present.† The filter is then put to dry in the steam-oven.

The dry precipitate is detached from the filter and transferred to a Rose's crucible‡ (previously heated and weighed). The paper is

* The filtrate may be tested to see if any copper is thus escaping into the solution by passing sulphuretted hydrogen through a portion of it.

† By double decomposition sulphuric acid will have been formed, and if this is not washed out the paper will become charred when it is dried in the steam-oven.

‡ This is a porcelain crucible provided with a perforated lid, through which a porcelain tube can be passed, by means of which the contents of the crucible

then incinerated in the usual way, and added to the precipitate. A little powdered sulphur (purified by redistillation) is introduced into the crucible, which is then covered with its perforated lid. A gentle stream of dry hydrogen is allowed to flow through the bent porcelain tube (Fig. 48), which is then inserted into the hole in the lid until the flange upon the tube rests upon the lid. The crucible is first gently heated until the sulphur is nearly all burnt off, when the temperature is raised to a bright-red heat and maintained at this point for about ten minutes. The apparatus is then allowed to cool, with the hydrogen still passing through it, until it is nearly cold, when it is removed to the desiccator, and after becoming quite cold is weighed.

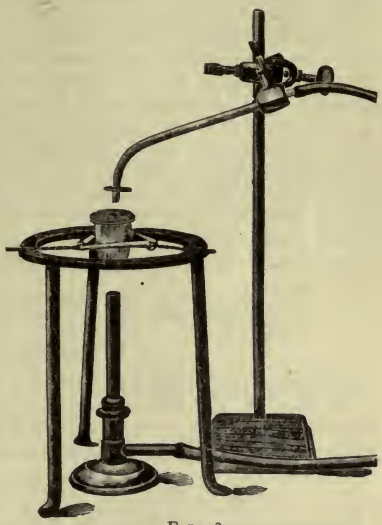

FIG. 48.

The operation is repeated, with the addition of a little more sulphur, until the weight is practically constant.

Cuprous thiocyanate, $Cu_2(CyS)_2$. Copper may also be precipitated as cuprous thiocyanate, which can be afterwards converted into cuprous sulphide, Cu_2S, by the action of heat in an atmosphere of hydrogen in a Rose's crucible; or it may be weighed on the filter as cuprous thiocyanate.

The solution of the copper salt, which should be slightly acidified with hydrochloric acid, is first saturated with sulphur dioxide* (see

can be heated in an atmosphere of hydrogen. In the absence of such an apparatus, an ordinary porcelain crucible may be used; and a common clay tobacco-pipe (of such a size that the mouth of the inverted bowl will just pass into the crucible) may be substituted for the perforated flange and tube. Hydrogen from a cylinder of compressed gas is most convenient. If the gas has to be generated from sulphuric acid and zinc, it must be dried before entering the crucible, by being passed through strong sulphuric acid. By arranging the flow of gas through the tube *before* introducing it into the crucible, there is no risk of projecting the contents out by too suddenly admitting the gas. Although not so advantageous, coal-gas may be employed instead of hydrogen.

* Or a solution containing equal weights of hydrogen ammonium sulphite and ammonium thiocyanate may be used to precipitate the copper salt.

note on p. 229). A solution of ammonium thiocyanate is then added until precipitation is complete, and the mixture heated nearly to the boiling-point for a few minutes. The precipitate, which is coloured when it is first formed, quickly becomes white, and settles very readily. It is washed with warm water by decantation two or three times, and then transferred to the filter, where it is washed until the wash-water is free from the acid of the original copper salt (*e.g.* sulphuric acid if copper sulphate is employed for the estimation). The precipitate is then dried in the steam-oven. The dry precipitate is then treated as described above in the case of copper sulphide, and finally weighed as cuprous sulphide.

As an alternative method, the precipitated cuprous thiocyanate may be filtered upon a weighed filter-paper, and dried in a hot-air oven at a temperature of 110° to 115°, and finally weighed as cuprous thiocyanate, the heating being repeated until the weight is constant. The compound retains water very persistently. Factor—

$$(Cu_2(CyS)_2)\ 242{\cdot}6 : (Cu_2)\ 126{\cdot}6 = 1 : 0{\cdot}52184$$

Silver.

Epitome of Process.—Silver is precipitated from solutions of its salts in the form of silver chloride, AgCl, by means of hydrochloric acid, and weighed in this form.* The filter is incinerated apart from the precipitate, with special precautions. Factor—

$$(AgCl)\ 143{\cdot}16 : (Ag)\ 107{\cdot}66 = 1 : 0{\cdot}75202$$

Estimation of Silver in Silver Nitrate, $AgNO_3$.—Use about 0·5 gram. The purified salt is weighed out into a beaker, and dissolved in cold water, and the solution acidified with a little nitric acid. Dilute hydrochloric acid is then gradually added, with continued stirring, until precipitation is complete. This point is easily determined, as the precipitated silver chloride coagulates and settles very quickly, so that it is easy to see when the addition of acid produces no further precipitation. The mixture is heated nearly to the boiling-point, and then allowed to settle. The precipitate is washed two or three times by decantation with boiling water acidified with nitric acid, after which it is transferred to the filter, and washed with hot water until the filtrate is free from hydrochloric acid, as indicated by the addition of silver nitrate. It is then placed in the steam-oven to dry.

* Silver is sometimes precipitated and weighed as silver bromide. The precipitation is effected by means of a solution of ammonium bromide, as hydrobromic acid is not a usual laboratory reagent. For the same reason the filter ash is treated as described in the alternative method, No. 2, for the chloride, given above. Owing to the greater weight of bromide, the experimental error is more equally divided between the silver and the halogen than in the case of the chloride.

The dry precipitate is detached from the paper as thoroughly as possible and transferred to a *porcelain* crucible, which with its lid has been previously heated and weighed. The paper is then folded up with the soiled parts innermost, and incinerated in a platinum coil. The greatest care must be taken to arrange the folding of the paper and the binding of the wire round it in such a way that neither the silver chloride nor the reduced silver comes in contact with the heated wire; otherwise the platinum will become alloyed with silver, and the analysis will be vitiated.

The filter ash is deposited in the inverted lid of the crucible, where it is moistened with a single drop of strong nitric acid, allowed to fall upon it by means of a pipette. The reduced silver is thereby converted into the nitrate. With a similar pipette a single drop of hydrochloric acid is added, which reproduces silver chloride. The crucible lid is then cautiously heated upon a pipeclay triangle by means of a small flame placed at a considerable distance below it, until the acids are completely evaporated.

The crucible is then gently heated until the precipitate just begins to melt, when it is removed along with the lid to the desiccator, and weighed when cold.*

Formula weight of silver nitrate = 169·66 theoretical percentage of Ag = 63·45.

Alternative Methods of Treating the Filter.†—1. After the precipitate has been transferred to the crucible, the latter is heated until the silver chloride just begins to fuse. The filter is then rolled up and incinerated as described above, and the ash allowed to fall into the crucible. It is then moistened with the acids as already explained, and the crucible again heated; at first very gently, to expel the excess of acid, afterwards to the point at which the silver chloride begins to melt. The crucible is then cooled and weighed.

2. The precipitate is transferred to the crucible, which is then heated until the chloride begins to fuse. The crucible is cooled in the desiccator and weighed.

The filter is then burnt as before, and the ash deposited in the crucible, which is once more gently heated, cooled, and weighed. The increase in weight is made up of the weight of the ash *plus* the

* The fused silver chloride may afterwards be removed from the crucible by adding a little dilute sulphuric acid, and introducing a fragment or two of granulated zinc. The chloride is thereby reduced to metallic silver, and the mass becomes detached from the porcelain.

† A third alternative process is similar to that given for lead, Method A, p. 241.

weight of a small quantity of metallic silver. This weight of silver is added to the amount which, by calculation, is found to be present in the silver chloride already weighed. The following example will make clear the process of calculating the result:—

Weight of silver nitrate taken	0·292 gram
Crucible + AgCl	21·7265 grams
Crucible alone	21·4850 ,,
Weight of AgCl	0·2415

Multiplying this result by the factor, the weight of metallic silver it contains is obtained—

$$0{\cdot}2415 \times 0{\cdot}75202 = 0{\cdot}181612 \text{ gram of Ag}$$

Crucible + AgCl + ash + reduced silver	21·73067
Crucible + AgCl ... ... 21·7265	
Ash ... ... 0·00017	
	21·72667
Weight of reduced silver	0·004

Therefore total silver = 0·181612 + 0·004 = 0·185612 gram

and $\frac{0{\cdot}185612 \times 100}{0{\cdot}292} = 63{\cdot}5$ per cent. of silver

Lead.

I. As Lead Oxide.

Epitome of Process.—The lead is precipitated from solutions of its salts in the form of basic carbonate, by means of ammonium carbonate. The basic carbonate is subsequently converted into plumbic oxide, PbO, by heat, and the metal is weighed in this form. Factor—

$$(PbO)\ 223 : (Pb)\ 207 = 1 : 0{\cdot}92825$$

Estimation of Lead in Lead Acetate, $Pb(C_2H_3O_2)_2{,}3H_2O$. —Employ about 0·75 gram. The recrystallised salt is weighed out into a beaker, and dissolved in water with the addition of a few drops of acetic acid. The mixture is slightly warmed, and a solution of ammonium carbonate containing a little ammonia is added, until precipitation is complete. Excess of the reagent is detrimental, as the precipitated lead carbonate is somewhat soluble in ammoniacal solutions. The solution should be allowed to become cold before being filtered. The precipitate is washed upon the filter with cold water until a drop of the filtrate gives no alkaline reaction with turmeric paper, and afterwards dried in the steam-oven.

The further treatment of the dry precipitate is carried out by either of the two following methods :—

(*a*) The precipitate is detached from the filter and carefully deposited upon a small clock-glass, and covered with an inverted beaker or funnel for protection. The filter is then folded up and placed in a porcelain crucible, which is heated until the paper is completely burnt. When it has again cooled, the ash is moistened with a drop or two of strong nitric acid from a pipette, after which it is gently warmed to expel the excess of acid. (In this way the reduced lead is converted into lead nitrate, which in the subsequent heating is decomposed into the oxide.) The precipitate upon the clock-glass is then carefully transferred to the crucible, by means of a small camel's-hair brush or a feather, in the manner shown in Fig. 49; after which the crucible is heated by means of a Bunsen flame to a dull-red heat for about ten minutes. It is then placed in

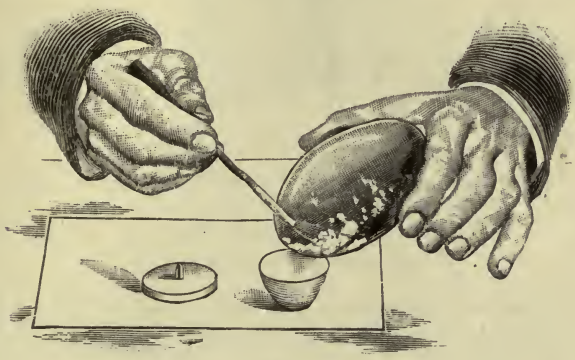

Fig. 49.

the desiccator to cool, and weighed. The heating is repeated until the weight is constant, care being taken not to raise the temperature sufficiently high to fuse the lead oxide.

(*b*) The precipitate is transferred at once to the porcelain crucible. The filter is cut into about three pieces, cutting from the apex of the cone to the upper edge with a clean sharp pair of scissors. Each piece is then separately burnt by holding it with a pair of tongs over the inverted crucible-lid, supported on a pipe-clay triangle, in the manner shown in Fig. 50. The ash is then moistened upon the crucible-lid with a drop of nitric acid, and the lid is gently warmed to expel the excess of acid. The crucible and lid are together heated until the precipitate is completely converted into the oxide as in the previous description.

Formula-weight of $Pb(C_2H_3O_2)_2,3H_2O = 379$. Theoretical percentage of Pb = 54·617.

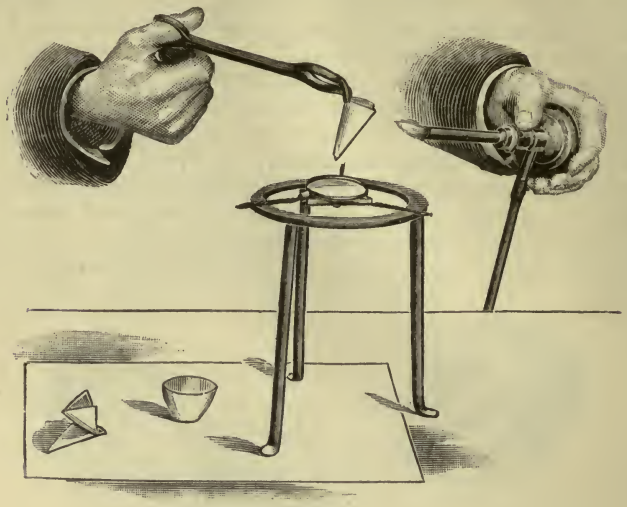

Fig. 50.

II. As Lead Sulphate.

Epitome of Process.—The lead is precipitated as lead sulphate, $PbSO_4$, by means of sulphuric acid, in the presence of a considerable volume of alcohol. The precipitate is dried and weighed. Factor—

$$(PbSO_4)\ 303 : (Pb)\ 207 = 1 : 0{\cdot}683\,16$$

Estimation of Lead in Lead Acetate, $Pb(C_2H_3O_2)_2,3H_2O$. —Employ from 0·5 to 0·75 gram. The salt is dissolved in rather less water than the usual quantity, in order to keep the solution moderately strong (about 80 c.c. will be found convenient). Dilute sulphuric acid is added until no further precipitate is produced. A moderate excess of the reagent is advantageous, since lead sulphate is less soluble in dilute sulphuric acid than in water. The precipitation is made complete by the addition of a quantity of alcohol (methylated spirit may be used) equal to about twice the volume of the aqueous solution (about 200 c.c.). After the precipitate has settled, it is transferred to a filter, and washed with methylated spirit (in which lead sulphate is quite insoluble)

until the filtrate is free from sulphuric acid, as shown by the addition of barium chloride to a few drops of the liquid. The precipitate is then dried in the steam-oven.

The filter is incinerated according to either of the two methods described in the foregoing estimation. The ash, however, after being moistened with nitric acid, is treated with a single drop of sulphuric acid in order to convert the lead nitrate first formed into lead sulphate. After the excess of the acids has been evaporated, the crucible is heated to dull redness, cooled in the desiccator, and weighed; the heating being repeated until the weight is constant.

Zinc.

I. As Zinc Oxide.

Epitome of Process.—The zinc is precipitated from solutions of its salts in the form of basic zinc carbonate * by means of sodium carbonate. The zinc carbonate is afterwards converted by heat into zinc oxide, ZnO, in which form the metal is weighed. Factor—

$$(ZnO)\,81 : (Zn)\,65 = 1 : 0{\cdot}80247$$

Estimation of Zinc in Zinc Sulphate, $ZnSO_4,7H_2O$.—Employ from 0·75 to 1 gram. The recrystallised salt is weighed out and dissolved in a beaker † in the usual manner. The solution is heated to boiling, and a solution of sodium carbonate is gradually added until precipitation is complete. The reagent should be carefully added, so as to avoid the loss of any of the solution by the undue rapidity of the effervescence due to the escape of the carbon dioxide. The mixture is boiled in the covered beaker for a few minutes, after which the precipitate is allowed to settle. It is washed with boiling water by decantation two or three times, and is then transferred to the filter. The washing is continued, with boiling water, until a few drops of the filtrate give no precipitate when gently warmed with a little barium chloride.

With the final washings the precipitate is collected together as much as possible into the apex of the filter.

The dried precipitate is transferred from the filter to a *porcelain* crucible (previously heated and weighed), special care being taken —by rubbing the sides of the filter one against the other—that the least possible quantity of the precipitate is left adhering to the paper. During the process of incineration, the zinc oxide is liable to become

* For the composition of this precipitate, see p. 55.
† See note, p. 223.

reduced to the metallic state, and the metal so formed to burn away and be lost. In order, as far as possible, to prevent this loss by facilitating the combustion of the paper, the filter (after the removal of the precipitate) may be moistened with a little solution of ammonium nitrate, and again placed *for a short time* in the steam-oven to dry.* It is then rolled up in platinum wire and burnt, the lamp-flame being only momentarily applied to it, so as to avoid unnecessary contact with the reducing gases of the flame. The ash is allowed to fall into the crucible, which is then heated to redness for ten minutes, with the lid upon it, over a Bunsen flame.† After cooling in the desiccator it is weighed, and the heating repeated until the weight is constant.

Formula-weight of $ZnSO_4,7H_2O = 287$. Theoretical percentage of Zn = 22·648.

II. As Zinc Sulphide.

Epitome of Process.—The zinc is precipitated from its solutions by means of ammonium sulphide as zinc sulphide, ZnS. The precipitate is dried, and heated in a stream of hydrogen in a Rose's crucible, and the metal is weighed as ZnS. Factor—

$$(ZnS)\,97 : (Zn)\,65 = 1 : 0{\cdot}6701$$

Estimation of Zinc in Zinc Sulphate, $ZnSO_4,7H_2O$.—Take about 0·75 gram. The salt is dissolved in warm water in a beaker, and a moderate quantity of ammonium chloride is added.‡ Colourless ammonium sulphide is then added until precipitation is complete. The mixture is boiled for a short time in order to cause it to coagulate, and therefore to settle more easily. It is washed twice by decantation with hot water containing a little ammonium sulphide, and then transferred to the filter, where the washing is continued with the same liquid until the filtrate is free from sulphates. The final washing should collect the precipitate as much as possible in the apex of the paper. The precipitate is dried in the steam-oven, after which it is transferred to a Rose's crucible. The filter is incinerated, with the precautions given above, and the ash added to the precipitate. A little powdered sulphur (redistilled) is sprinkled into

* If the precipitate has been detached cleanly from the paper, this operation may be omitted.

† When heating a crucible containing compounds of easily reduced metals, the lamp should be placed at such a distance beneath the crucible that the flame does not envelop it and lick over the top; otherwise reduction of the compound by the heated gases from the flame is liable to result; and in such a case as zinc, portions of the metal itself would be volatilised, and therefore lost.

‡ In general analyses, if the solution containing the zinc salt is acid, it is first rendered slightly alkaline by the addition of ammonia.

the crucible, the lid is put on, and a gentle stream of hydrogen is passed into the apparatus (see note, p. 237). The crucible is first gently heated, the temperature being gradually increased to a bright-red heat, using a blowpipe if necessary. It is then allowed to cool with the gas still passing, until nearly cold, when it is removed to the desiccator, and finally weighed. It is reheated with a little more sulphur in the same manner until the weight is uniform.

Manganese.

Epitome of Process.—The manganese is precipitated as manganous carbonate by means of sodium carbonate. The carbonate is afterwards converted by heat into the tetroxide, Mn_3O_4, in which form the metal is weighed. Factor—

$$(Mn_3O_4)\ 229 : (3Mn)\ 165 = 1 : 0{\cdot}7205$$

Estimation of Manganese in Potassium Permanganate, $KMnO_4$. — Employ about 0·75 gram. The powdered recrystallised salt is weighed out into a beaker and dissolved in water. A stream of sulphur dioxide is passed through the solution until the liquid is perfectly colourless and clear.* The manganese is then precipitated and washed exactly as described for zinc (p. 243). In this case, however, two special sources of error arise. First, the precipitation of the manganese is never quite complete, causing, therefore, a *loss;* and, second, the precipitate always carries down with it a certain quantity of the alkali, thus giving rise to *gain.* Although by chance these two errors might neutralise each other, an exact result can only be certainly obtained by adopting the special methods for their elimination given below.

The filtrate, together with the whole of the wash-water, is evaporated to dryness in a platinum, nickel, or porcelain dish. The evaporation may be conducted at first over a rose burner, provided the flame be so adjusted that the liquid never actually boils. But when the liquid reaches such a state of concentration that salts begin to deposit, the process must be finished upon a steam-bath. During the entire process care must be taken that no particles of foreign matter fall into the dish ; it is therefore desirable

* This roundabout method of obtaining a solution of manganous sulphate is preferred to the direct use of the crystallised sulphate, for the reason that the latter salt is not easy to obtain in a definite state of hydration. According to the conditions of crystallisation, manganous sulphate forms various hydrated salts. Thus, if deposited below $-6°$, the crystals contain $7H_2O$; between $7°$ and $20°$ the salt contains $5H_2O$; while between $20°$ and $30°$ it contains $4H_2O$. When manganous sulphate is used, the latter salt is the best to employ. It is prepared by evaporating the solution at a temperature about $25°$.

to screen the vessel, either by supporting over it a sheet of filter-paper by means of a glass tube or rod bent into a triangle and held by a clamp, as shown in Fig. 51; or by supporting a large inverted funnel over the dish, taking care that the water which condenses upon the funnel shall drip outside the dish.

The residue is then treated with a little hot water, which dissolves the salt, leaving any manganese present in the form of the hydrated oxide. This is filtered through a *separate filter*, washed with hot water until the wash-water is free from sulphates, and then placed in the steam-oven to dry.

FIG. 51.

The contents of the two filters are next transferred to a platinum crucible, and the two filter-papers incinerated in a coil of platinum wire, one after the other, and the two ashes deposited in the crucible. The crucible is then raised to a bright-red heat for about ten minutes (see note, p. 244); then cooled in the desiccator and weighed.*

The residue in the crucible is treated with a little boiling water, the particles being reduced to powder by means of a short piece of stout glass rod with smooth ends. The water is poured off through a filter, and the residue washed in this way by decantation three or four times. It is then entirely transferred to the filter, and thoroughly washed with hot water until the washings cease to give a pronounced yellow coloration to the flame when heated upon a loop of clean platinum wire. The residue is then dried in the steam-oven, and afterwards transferred to the crucible; the filter is incinerated, and the crucible again strongly heated, allowed to cool in the desiccator,

* Weighing at this stage is not *necessary*. By doing so, however, the student will ascertain the extent of the error which is due to the presence of alkali in the precipitate, and will therefore be able to judge of the value of the next operation.

and weighed. The heating is repeated until the weight remains constant.

In calculating the result, it must be remembered that the ash from *three* filters has to be deducted from the weight.

Formula-weight of $KMnO_4$ = 158. Theoretical percentage of Mn = 34·81.

Nickel.

Epitome of Process.—The nickel is precipitated as nickelous hydroxide, $Ni(HO)_2$, by means of potassium hydroxide. The dried precipitate is converted by heat into nickelous oxide, NiO, in which form the metal is weighed. Factor—

$$(NiO)\,75 : (Ni)\,59 = 1 : 0{\cdot}78666$$

The precipitation is conducted as in the case of copper (p. 235 ; see also note, p. 222). The filter is incinerated in a platinum coil, and the precipitate is strongly heated in a platinum crucible (avoiding the entrance of reducing gases from the flame, see p. 244) until the weight is constant.

Nickelous hydroxide retains traces of the alkali with some persistence ; therefore, when special exactness is desired, the precipitate is afterwards treated as in the case of manganese.

A convenient salt in which to make an estimation of nickel is the double ammonium nickel sulphate, $(NH_4)_2SO_4,NiSO_4,6H_2O$. Formula-weight = 395. Theoretical percentage of Ni = 14·93.

Cobalt.

Epitome of Process.—The cobalt is precipitated as hydroxide, $Co(HO)_2$, by means of potassium hydroxide. The dried precipitate is reduced in a stream of hydrogen in a Rose's crucible, and weighed in the metallic state.

The precipitation is carried out as in the case of nickel. The filter is incinerated in a porcelain crucible along with the precipitate, after which a gentle stream of dry hydrogen is delivered through the Rose's apparatus (p. 237), and the precipitate heated to a low red heat in the gas for about ten minutes. It is allowed to cool in the hydrogen atmosphere, and then weighed.

Like the hydroxides of nickel and of manganese, cobalt hydroxide retains traces of alkali. The contents of the crucible must therefore be treated with hot water until the washings are free from alkali. The residue is again dried, and once more heated in a stream of hydrogen.

Potassium.

I. As Potassium Sulphate.

Epitome of Process.—The potassium salt is converted into potassium sulphate, K_2SO_4, by treatment with strong sulphuric

acid. The mixture is evaporated to dryness and strongly heated, and the dry residue of potassium sulphate weighed. The process is only applicable in the case of compounds of potassium with volatile acids which will be completely expelled by the sulphuric acid, leaving nothing but the potassium sulphate. Such compounds, for example, as the nitrate, chloride, bromide, etc. Factor—

$$(K_2SO_4)\ 174 : (2K)\ 78 = 1 : 0{\cdot}44827$$

Estimation of Potassium in Potassium Nitrate, KNO_3, —Take about 0·5 gram. The nitre (purified by recrystallisation) is weighed out into a platinum crucible, and a few drops of strong sulphuric acid are added.* The crucible is then supported in an inclined position upon the pipe-clay triangle, the lid being placed so that the crucible is very nearly but not entirely closed, as shown in Fig. 52. A gentle heat is applied to the crucible, the flame being placed under the edge of the vessel. After the nitric acid has been expelled, the excess of sulphuric acid begins to volatilise, as seen by the escape of white fumes.

Fig. 52.

As the operation proceeds, the hydrogen potassium sulphate, which is the first product of the action, and which is a moderately easily fusible salt, is converted into the normal sulphate with elimination of sulphuric acid. The normal salt being much more difficult of fusion, the contents of the crucible gradually become pasty, and finally solid. During this stage, care must be taken that no loss by spirting takes place.

The completion of this change requires prolonged exposure to a bright-red heat, but in an atmosphere charged with ammonia it takes place much more quickly. Hence, while the mass is heated to a dull red, a few small fragments of ammonium carbonate are introduced from time to time, the lid being replaced immediately. The heat is continued for a few minutes after the addition of the

* In the case of potassium salts containing acids which are expelled with effervescence, the salt should be first moistened with water, and the sulphuric acid added drop by drop so long as effervescence takes place, the cover being replaced immediately after each addition of acid.

ammonium carbonate, and the crucible cooled in the desiccator and weighed. It is afterwards re-heated with a little more of the carbonate and again weighed, the operation being repeated until the weight is constant.

Formula-weight of KNO_3 = 101. Theoretical percentage of K = 38·61.

II. As Potassium Platinic Chloride, $2KCl,PtCl_4$.

Epitome of Process.—The potassium is precipitated in the form of the double chloride of potassium and platinum (potassium chloroplatinate), and the precipitate is weighed without alteration upon a tared filter.

This process is only applicable in the case of such potassium compounds as are wholly converted into the chloride by means of hydrochloric acid. Factor—

$$(2KCl,PtCl_4)\ 486 : (2K)\ 78 = I : 0{\cdot}1605$$

Estimation of Potassium in Potassium Chloride, KCl. —Employ about 0·25 gram. The recrystallised salt is weighed out into a small porcelain dish, and dissolved in about 10 c. c. of water, to which two or three drops of hydrochloric acid have been added. A moderately strong solution of platinum chloride is added in slight excess,* and the mixture evaporated on a steam-bath until it becomes semi-solid.

The crystalline residue is rinsed with alcohol, and, after being allowed to settle, the supernatant liquid is poured off through a previously weighed filter (see p. 194). The precipitate is washed by decantation with alcohol two or three times, and finally transferred to the filter, where it is further washed with alcohol (contained in a small wash-bottle) until the filtrate is free from any tinge of yellow colour. The filter is then withdrawn from the funnel, carefully folded, and placed between a pair of watch-glasses to dry in the steam-oven. It is then heated and weighed until the weight is constant.†

Formula-weight of potassium chloride, KCl = 74·5. Theoretical percentage of K = 52·349.

* It is desirable that the strength of the solution of platinum chloride should be approximately known, in which case a quantity of it will be added which contains a weight of $PtCl_4$ equal to about four times the weight of potassium chloride taken for the analysis. The solution should be strong, so as to avoid unnecessary loss of time in evaporation. If the strength of the platinum chloride is unknown, it is only possible to ascertain whether excess has been added by observing whether the supernatant liquid, as it becomes concentrated by evaporation, has the yellow colour of the reagent.

† For an alternative method of treating the precipitate, see Estimation of ammonium below.

Ammonium.

Epitome of Process.—The ammonium salt is first boiled with sodium hydroxide, and the ammonia which is thus expelled is absorbed by dilute hydrochloric acid. The ammonium, in the ammonium chloride so obtained, is then precipitated as the double chloride of ammonium and platinum, $2NH_4Cl,PtCl_4$, by means of platinic chloride, and is finally weighed in this form. Factor—

$$(2NH_4Cl,PtCl_4)\ 644 : (2NH_4)\ 36 = 1 : 0{\cdot}08108$$

Estimation of Ammonium in Ammonium Sulphate, $(NH_4)_2SO_4$.—Employ about 0·25 gram. The purified salt is weighed out into a flask (F, Fig. 53), and dissolved by the addition of a small quantity (30 to 40 c.c.) of water. The rubber cork, carrying a dropping-funnel and leading-tube, is then introduced; the drawn-out end of the funnel tube should nearly, but not quite, touch the surface of the liquid.

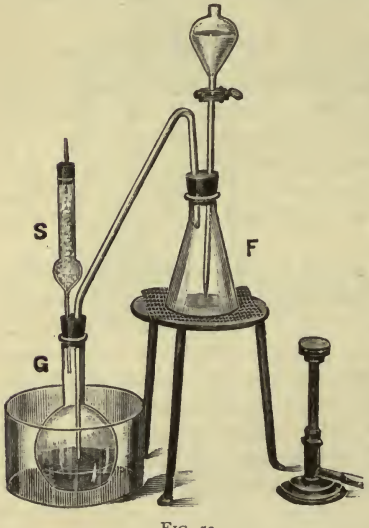

Fig. 53.

To the other end of the twice-bent leading-tube * the empty flask G is attached by means of a second rubber cork, through which passes the "scrubber" tube S, which is packed with small broken glass, previously thoroughly washed. The leading tube should be moderately wide in the bore, and at both ends it should be cut obliquely, as shown in the figure.†

When the apparatus is thus arranged, a quantity of dilute hydrochloric acid is introduced into the absorption flask G through the scrubber tube, in order to thoroughly wet the broken glass with the acid. While this is being done the tap of the funnel must be open, to allow the air

* It is preferable that the leading-tube should be in one piece, as shown in the figure, as every unnecessary joint is liable to introduce error through leakage.

† This is done in a few minutes by grinding the tube down upon a sheet of moderately coarse emery cloth, which is freely wetted with turpentine.

to pass out (which it will do if the funnel does not touch the liquid, as directed). When the acid is in, the obliquely cut end of the leading-tube should just dip into the liquid, so as to about half close the orifice. The tap is then closed, and the funnel about three-parts filled with a moderately strong solution of sodium hydroxide (1 part of soda to 5 parts of water).

The solution in flask F is heated nearly to the boiling-point, and the caustic soda allowed to enter from the funnel drop by drop, the liquid being gently boiled the whole time.* When the whole of the soda has been introduced, and the ammonia has been all expelled by continuing the boiling for a few minutes, the tap of the funnel is opened (the end now being beneath the surface of the liquid), and the gaseous contents of the flask are *very gently* drawn through into the absorption vessel by means of a piece of rubber tube attached to the scrubber tube. The apparatus is then disconnected, and the contents of the absorption flask are transferred to a porcelain dish. The end of the leading-tube, the scrubber, and the flask are thoroughly washed with water, and the washings added to the solution in the dish.

The requisite quantity of platinum chloride (see note, p. 249) is added, and the solution evaporated upon a steam-bath until it becomes semi-solid. The crystalline precipitate of $2NH_4Cl,PtCl_4$ is then washed with alcohol, and afterwards treated in one of the two following alternative ways :—

(*a*) It is transferred to a tared filter, dried, and weighed as described for the similar potassium compound.

(*b*) The precipitate is washed with alcohol by decantation, the washings being poured off through an unweighed filter. The process is continued until the decanted liquid is free from any tinge of yellow colour. The filter, which contains small quantities of the precipitate, is placed in the steam-oven to dry. The main portion of the precipitate is rinsed from the dish into a platinum crucible by means of a fine alcohol jet, and the crucible placed in the steam-oven to dry.

* Care must be taken throughout the whole of the boiling process that none of the alkaline liquid is carried over either as spray or by frothing. This precaution is specially necessary when the ammonia which is absorbed in the flask G is afterwards to be estimated by volumetric methods (*q.v.*). If the leading-tube is of moderately large bore, and is cut off diagonally as directed, the spray which is thrown up will run back. Should the mixture show any tendency to froth (which will not be the case with the particular example here chosen, but which is liable to happen with some ammoniacal liquids), a few fragments of paraffin wax should be added before commencing to boil.

In order to keep the absorption flask cool, it may with advantage be stood in a dish of water during the operation.

The crucible with its dry contents is then weighed, after which the filter is incinerated in a platinum coil, and the ash added. The crucible is then weighed again. The increase in weight is due to the ash *plus* a small quantity of metallic platinum derived from that portion of the precipitate which was carried on to the filter during the process of washing. This quantity must therefore be added to the weight of platinum which is found by calculation to be present in the precipitate in the crucible * (as explained in the case of silver, p. 240).

The result of the analysis may be checked by converting the whole of the precipitate into metallic platinum, and weighing it. The crucible is first gently heated by means of a small flame, and the temperature gradually raised to a bright-red heat, after which the crucible is cooled in the desiccator and weighed.

Formula-weight of $(NH_4)_2SO_4 = 132$. Theoretical percentage of $(NH_4) = 27{\cdot}27$.

Tin.

Epitome of Process.—The tin is precipitated as sulphide from either "stannous" or "stannic" solutions by means of sulphuretted hydrogen. The dried precipitate is afterwards converted by heating in contact with air, into tin dioxide, SnO_2, in which form the metal is weighed. Factor—

$$(SnO_2)\ 150 : (Sn)\ 118 = 1 : 0{\cdot}78666$$

Estimation of Tin in Stannous Chloride, $SnCl_2{,}2H_2O$. —Employ about 0·6 gram. The purified salt is weighed into a beaker, and dissolved in a small quantity of dilute hydrochloric acid. The solution is diluted by the addition of about 250 c.c. of moderately warm water, and sulphuretted hydrogen passed through until the liquid is saturated with gas. The beaker is then allowed to stand for an hour or two in a warm place, or it may be gently heated for a short time to a temperature not higher than can be comfortably borne by the hand. The precipitate has a great tendency to pass through the filter, especially during the process of washing. This is overcome to a great extent by employing a double filter, or by employing a dilute solution of ammonium acetate acidified with a little acetic acid, with which to wash the

* This method may be adopted as an alternative in the estimation of potassium. In that case, however, it is very important that the *least possible* quantity of the precipitate is carried on to the filter during the process of washing, for the reason that, unlike the ammonium compound, the potassium compound, when heated, leaves a residue of potassium chloride as well as metallic platinum.

precipitate. The dried precipitate is transferred to a porcelain crucible, and the filter incinerated in a platinum coil. The ash is moistened with a single drop of strong nitric acid, as in the case of copper (p. 235), and the excess of acid expelled by a gentle heat. The crucible is then *gradually* heated, first with its lid on, and afterwards with it removed, until the sulphide is completely converted into oxide ; the temperature being finally raised to a red heat by means of a blowpipe. The last traces of sulphur are expelled by allowing the crucible to partially cool, introducing a few fragments of ammonium carbonate, and again strongly heating until the weight is constant.

Formula-weight of $SnCl_2,2H_2O = 225$. Theoretical percentage of Sn = 52·44.

Arsenic.

I. As Arsenious Sulphide, As_2S_3.

Epitome of Process.—The arsenic is precipitated from a solution of an "arsenious" compound in the form of arsenious sulphide, As_2S_3, by means of sulphuretted hydrogen. The precipitate is weighed upon a tared filter. It is afterwards subjected to treatment with carbon disulphide to remove free sulphur. Factor—

$$(As_2S_3)\ 246 : (2As)\ 150 = 1 : 0{\cdot}60975$$

Estimation of Arsenic in Arsenious Oxide, As_4O_6.—Employ about 0·5 gram. The arsenious oxide (purified by resublimation) is weighed out into a conical flask capable of holding about half a litre, and fitted with a caoutchouc cork carrying two tubes for the transmission of a stream of gas through the solution, the longer tube reaching nearly to the bottom of the flask.

The arsenious oxide is dissolved in a small quantity (30 to 40 c.c.) of dilute hydrochloric acid, the operation being aided by gently warming the mixture upon a steam-bath. The solution must not be boiled. When the oxide has entirely dissolved, the liquid is largely diluted by the addition of about 200 c.c. of warm water, and a gentle stream of sulphuretted hydrogen passed through, until precipitation is complete.

Precipitated in this manner from a warm solution, the arsenious sulphide settles quickly, and is easily filtered.* The excess of

* When conditions exist which cause the precipitation of sulphur, such as the presence of arsenic acid, chromates, ferric salts, etc., the solution should be cold, or only slightly warm, as from a hot solution the sulphur is deposited in coagulated particles, and in this form it is much more difficult to dissolve in carbon disulphide. In this case the filter containing the dried precipitate must be digested with carbon disulphide in a dish upon a water-bath. The carbon disulphide must itself be free from dissolved sulphur, and should leave no residue when a small quantity of it is evaporated upon a watch-glass.

sulphuretted hydrogen is expelled from the solution by passing a brisk stream of carbon dioxide through the still warm solution, after which the precipitate is transferred to a weighed filter, and washed with warm water containing a little sulphuretted hydrogen. If any of the precipitate has deposited itself upon the glass tube delivering the sulphuretted hydrogen, it may be dissolved off by means of ammonia in a small test-tube, and reprecipitated by the addition of hydrochloric acid, and added to the main portion. The precipitate, after being washed until the washings are free from hydrochloric acid, is dried in the steam-oven, and weighed in a stoppered tube (p. 194).

The filter is then carefully replaced in the funnel, and the precipitate rinsed with small quantities of carbon disulphide, until a few drops of the liquid, when evaporated upon a watch-glass, leave no residue. It is then once more dried and weighed.

Formula-weight of $As_4O_6 = 396$. Theoretical percentage of As = 75·75.

II. As Magnesium Pyro-arsenate, $Mg_2As_2O_7$.

Epitome of Process.—The arsenic is precipitated from solutions of "arsenic" * compounds in the form of ammonium magnesium arsenate, $(NH_4)MgAsO_4,6H_2O$, by means of magnesium sulphate in the presence of ammonia and ammonium chloride. The precipitate is converted by heat into magnesium pyro-arsenate, $Mg_2As_2O_7$, in which form the arsenic is weighed. Factor—

$$(Mg_2As_2O_7)\ 310 : (2As)\ 150 = 1 : 0{\cdot}4838$$

Estimation of Arsenic in Hydrogen Disodium Arsenate, $HNa_2AsO_4,12H_2O$.—Employ about 0·75 gram. The recrystallised salt is weighed out into a wide-mouth stoppered bottle, about 500 c.c. capacity, and dissolved in cold water. A moderate quantity of ammonia is added, and then "magnesia mixture" † in excess. The mixture is then briskly shaken in the stoppered bottle for about five minutes, after which it is filtered, washed, and dried, exactly as directed for the treatment of magnesium phosphate (p. 233).

The dried precipitate is detached from the filter and deposited upon a clock-glass, or a piece of black glazed paper, and covered

* "Arsenious" compounds must be first oxidised to the "arsenic" condition by gently warming the solution with strong hydrochloric acid, and adding a few crystals of potassium chlorate. The liquid is kept at a gentle heat until it no longer smells of chlorine, and then rendered alkaline by the addition of ammonia.

† See Reagents, in the Appendix.

over with a clean beaker. The filter is then moistened with a few drops of solution of ammonium nitrate, and returned to the steam-oven. As soon as it is dry,* it is incinerated in a porcelain crucible, the temperature being gradually raised to a bright-red heat. The crucible is then allowed to cool, and the precipitate transferred to it (see p. 241), after which it is heated in a gentle stream of oxygen by means of Rose's apparatus. The heat, which is applied very gradually at first, is finally increased to bright redness. After being cooled and weighed, it is reheated in oxygen until the weight is constant.

Formula-weight of $HNa_2AsO_4,12H_2O = 402$. Theoretical percentage of As = 18·65.

Antimony.

Epitome of Process.—The antimony is precipitated as antimonious sulphide, Sb_2S_3, by means of sulphuretted hydrogen. The precipitate, which retains water after drying in the steam-oven, and which also usually contains free sulphur, is treated by one of the following methods :—

(*a*) It is freed from water and sulphur by being heated in a porcelain boat in a stream of carbon dioxide, and weighed as Sb_2S_3; or

(*b*) It is converted into the tetroxide, Sb_2O_4, by treatment with strong nitric acid, and weighed in this form.† Factors—

$$(Sb_2S_3)\ 336 : (2Sb)\ 240 = 1 : 0{\cdot}71428$$
$$(Sb_2O_4)\ 304 : (2Sb)\ 240 = 1 : 0{\cdot}78947$$

Estimation of Antimony in Tartar Emetic, $(SbO)K(C_4H_4O_6)$. Employ about 0·75 gram.—The dried salt is weighed into a conical flask, and dissolved in a little water. Three or four grams of tartaric acid, dissolved in a little water, are added, and then a few drops of hydrochloric acid. The solution is then diluted by the addition of about 200 c.c. of slightly warm water (if sufficient tartaric acid has been introduced, this dilution will not cause any precipitation), and a slow stream of sulphuretted hydrogen passed through, as described in the case of arsenic (p. 253). When the solution is saturated with the gas, the exit and delivery tubes may be joined by means of a piece of rubber tube, in order to prevent the entrance of air, and the flask is allowed to stand in a warm place for an hour or two.

The excess of sulphuretted hydrogen is then expelled by passing

* If left too long in the oven, the ammonium nitrate is expelled, and the object for which it is added, namely, to aid the combustion of the paper, will be defeated.

† This latter method is preferable in cases where the quantity of antimony is small.

a brisk stream of carbon dioxide through the mixture, which may at the same time be gradually heated to the boiling-point.* The precipitate is transferred to a weighed filter, and washed as quickly as possible (without allowing the filter to run dry) with hot water containing a little sulphuretted hydrogen. It is then dried in the steam-oven until the weight is constant.

The precipitate, consisting of Sb_2S_3 *plus* an unknown quantity of water and free sulphur, is treated in one of the following ways:—

(*a*) A certain proportion of it (as much as convenient) is transferred to a porcelain boat which has previously been heated and weighed, and the boat with its charge again weighed. The boat is then pushed, by means of a glass rod, into a wide glass tube about 25 c.c. (10 inches) long, supported in a horizontal position, and a gentle current of dry carbon dioxide passed over it. The boat is gently heated by means of a Bunsen flame in the stream of gas, whereby the water and the sulphur are expelled from the precipitate. The tube is allowed to cool with the gas still passing through, after which the boat containing its residue of black anhydrous Sb_2S_3 is withdrawn and weighed.†

From the loss of weight the contents of the boat have suffered by this treatment, the quantity of pure Sb_2S_3 which was present in the *whole* of the original precipitate can be deduced, and from this the amount of antimony can be calculated.

(*b*) A certain proportion of the precipitate is transferred to a weighed porcelain crucible, and the crucible with the precipitate again weighed.‡ It is moistened by the addition of three or four drops of ordinary strong nitric acid (sp. gr. 1·42), and the crucible covered with an inverted lid. By means of a pipette 3 or 4 c.c. of fuming nitric acid (sp. gr. 1·5) are introduced, the lid being drawn slightly aside and quickly replaced. Rapid oxidation of the antimony sulphide and free sulphur immediately takes place, after which the contents of the crucible are evaporated to dryness upon a steam-bath.

The crucible is then heated by means of a Bunsen flame, at

* Since antimonious sulphide is decomposed by boiling hydrochloric acid, this operation would not be safe if much acid were present.

† A small portion of the original dried precipitate may be tested for free sulphur by heating it in a test-tube with a little strong hydrochloric acid. If it entirely dissolves to a perfectly clear liquid, no sulphur is present, in which case the portion which is treated in the boat will only require to be very gently heated to expel the water.

‡ In cases where the total precipitate is very small, the filter with its entire contents is transferred to the crucible. In such a case the filter-ash must be deducted from the final weight.

first very gently, whereby sulphuric acid is expelled, and antimony tetroxide, Sb_2O_4, is left. The crucible is cooled in the desiccator, and weighed; the heating being repeated until the weight remains constant. From this result the weight of antimony tetroxide which would be yielded by the *whole* of the precipitated sulphide can be calculated, and therefrom the weight of antimony.

Formula-weight of $(SbO)K(C_4H_4O_6) = 323$. Theoretical percentage of Sb = 37·15.

Cadmium.

Epitome of Process.—The cadmium is precipitated as cadmium sulphide, CdS, by means of sulphuretted hydrogen. The precipitate is dried, and weighed upon a tared filter. Factor—

(CdS) 144 : (Cd) 112 = 1 : 0·7777

The precipitation is conducted in a beaker, from a solution acidified with hydrochloric acid. The precipitate is first washed with water containing a little sulphuretted hydrogen and a few drops of hydrochloric acid, and afterwards with plain water.

The dried precipitate, after weighing, is extracted with carbon disulphide to remove traces of free sulphur (see Arsenic, p. 254), and again dried and weighed.

Mercury.

Epitome of Process.—The mercury is precipitated in the form of mercuric sulphide, HgS, by means of sulphuretted hydrogen. The precipitate is dried, and weighed upon a tared filter. Factor—

(HgS) 232 : (Hg) 200 = 1 : 0·86206

The details of the operation are the same as in the case of cadmium.

SECTION III.

Typical Gravimetric Estimations of Acid Radicals.

Sulphuric Acid, (SO_4).

Epitome of Process.—The sulphuric acid radical is precipitated in the form of barium sulphate, $BaSO_4$, by means of barium chloride in the presence of hydrochloric acid. The precipitate is dried, and weighed in the same form.* Factor—

$$(BaSO_4)\ 233 : (SO_4)\ 96 = 1 : 0{\cdot}4120$$

Estimation of (SO_4) in Potassium Alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$.†—Employ about 0·5 gram. The salt is weighed out into a beaker, dissolved in water, and the solution heated to the boiling-point. A *small* quantity of hydrochloric acid is added, and then a little moderately strong solution of ammonium chloride. While the liquid is still boiling, a solution of barium chloride, heated to boiling in a large test-tube, is added until precipitation is complete. The precipitate is washed three or four times by decantation with hot water, and finally transferred to the filter, where it is washed until the filtrate is free from chlorides. The last washings should be made to collect the precipitate as much as possible into the apex of the filter, after which it is placed in the steam-oven to dry.

The dry precipitate is detached as completely as possible from the paper and transferred to a platinum crucible, and the filter incinerated in a platinum coil. The precipitate should be shaken slightly to one side in the crucible, so that the ash may be deposited in a clear space upon the bottom. By means of a fine pipette, the ash is moistened with a single drop of hydrochloric acid, in order to convert into barium chloride any sulphide which may have been

* Barium is estimated as $BaSO_4$ by precipitation with dilute sulphuric acid, the process being carried out as described above. Strontium is also estimated in the same manner, except that for the complete precipitation of $SrSO_4$ it is necessary to add a quantity of alcohol (methylated spirit) equal in bulk to the volume of the aqueous liquid.

† For the treatment of insoluble sulphates, see p. 184

formed by the reduction of a portion of the sulphate adhering to the paper. Then a drop of dilute sulphuric acid is similarly added, and the crucible very gently heated to expel the excess of the acids, after which the temperature is raised to a red heat. It is then cooled in the desiccator and weighed.*

Formula-weight of $K_2SO_4,Al_2(SO_4)_3,24H_2O = 948$. Theoretical percentage of $SO_4 = 40{\cdot}50$.

Chlorine in Chlorides †

Epitome of Process.—The chlorine is precipitated in the form of silver chloride, AgCl, by means of silver nitrate, and is weighed in this form. The filter is incinerated apart from the precipitate (see Silver, p. 238). Factor—

$$(AgCl)\ 142{\cdot}5 : (Cl)\ 35{\cdot}5 = 1 : 0{\cdot}2491$$

Estimation of Chlorine in Sodium Chloride, NaCl. Employ about 0·25 gram.

The process is carried out as in the estimation of silver, p. 238.

Formula-weight of $NaCl = 58{\cdot}5$. Theoretical percentage of $Cl = 60{\cdot}68$.

Carbon Dioxide.

I. Estimation by Difference.

Epitome of Process.—A known weight of the carbonate is decomposed by a suitable acid in a weighed apparatus, and the carbon dioxide expelled. The loss of weight which results, represents the carbon dioxide in the compound. Various forms of apparatus are used. Fig. 54 represents a simple apparatus which can readily be fitted up by the student himself, and which gives very good results. It consists of a small flask of thin glass fitted with a cork carrying a thistle funnel and a bent exit tube. The exit tube is drawn down to a moderately fine tube, which passes to the bottom of a small narrow test-tube, *t*. The portion

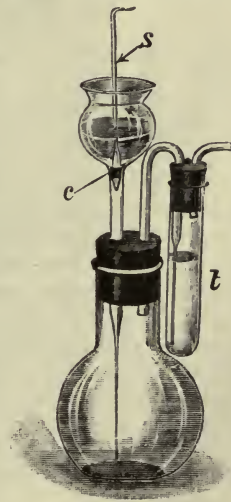

Fig. 54.

* In the estimation of (SO_4) as barium sulphate in general analysis, whether in a *sulphate*, or in a *sulphide* after oxidation into (SO_4), the following points must be borne in mind: nitric acid, nitrates, and chlorates must be absent; hydrochloric acid must not be present in large quantity.

† The estimation of bromine in bromides is carried out in the same manner, the precipitate being treated by the alternative method, No. 2, given on p. 239.

of the funnel tube which extends down into the flask is also drawn out. A short piece of small rubber tube is introduced into the thistle funnel at *c*, and a piece of drawn-out glass rod, *s*, pushed into this, serves as a stopper. Dilute acid (for decomposing the carbonate) is introduced into the funnel, and the tube *t* is half filled with strong sulphuric acid in order to arrest the escape of aqueous vapour along with the issuing carbon dioxide. By slightly lifting the little stopper *s*, the admission of acid can be regulated with considerable nicety.

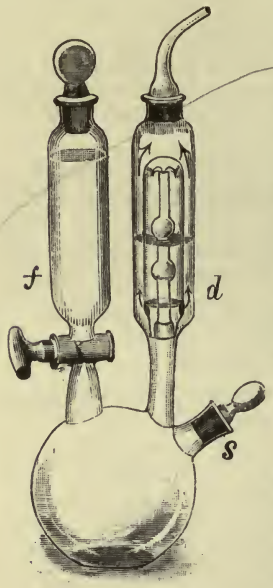

FIG. 55.

The apparatus shown in Fig. 55 (known as the Schrötter apparatus) possesses the advantage of not containing any corks. The carbonate is introduced at the stoppered neck *s*; the acid is admitted from the stoppered funnel *f*, while the escaping carbon dioxide is dried by its passage through the strong sulphuric acid contained in *d*. The gas passes up the central tube within *d*, as indicated by the arrows, and forces the acid down to the level of the holes near the bottom of the second tube, and then bubbles out through the acid and escapes at the top of the outer tube.

Estimation of CO_2 in Potassium Carbonate, K_2CO_3.—Employ about 1·5 gram. The pure dry salt is weighed into the flask of the apparatus, and the slightly greased stopper inserted in the neck *s*. The dropping-funnel is then nearly filled with dilute sulphuric acid, and the drying-tube is about half filled with strong oil of vitriol, and the apparatus carefully weighed. The acid from the funnel is then allowed to *very slowly* enter the flask, so that the carbon dioxide may escape in single bubbles through the strong acid in the drying-tube. If the bubbles pass in a stream faster than about two to the second (*i.e.* too quickly to be easily counted), the gas will not be deprived of aqueous vapour by the acid, and the result of the analysis will be vitiated. When the effervescence has ceased, the remainder of the acid is allowed to run in and the tap left open. The flask is then very gently heated over a *small* flame, in order to expel the whole of the carbon dioxide, until the liquid *just begins* to boil. During the heating, the gaseous contents of the

flask are *slowly* sucked out by means of an aspirator attached by a caoutchouc tube to the exit of the drying-tube. The aspirator shown on p. 204 may be employed, or the gas may be drawn out by the lungs. In the latter case, the peculiar sweet taste of the carbon dioxide makes it easy to tell when the whole of the gas has been withdrawn and its place taken by air. The aspiration must not be unnecessarily prolonged. The apparatus is then allowed to become cold, and afterwards weighed. While the apparatus is cooling, the exit tube of the drying-vessel *d* should be closed with a cap (consisting of a short piece of caoutchouc tube plugged at one end with a fragment of glass rod) in order to prevent the absorption of atmospheric moisture by the sulphuric acid ; the cap is removed while weighing.*

Formula-weight of $K_2CO_3 = 138$. Theoretical percentage of $CO_2 = 31{\cdot}88$.

II. Estimation by Direct Weighing.

Epitome of Process.—The carbonate is decomposed by an acid, and the evolved carbon dioxide is absorbed by soda-lime in a weighed apparatus.

Fig. 56 represents the apparatus which may be employed for the process. The carbonate is decomposed in the flask B by means of acid introduced from the dropping-funnel, the fine drawn-out end of which reaches nearly to the bottom. The carbon dioxide is first dried by passing through the tube E, containing pumice moistened with sulphuric acid. It is then deprived of acid vapours by means of the tube D, filled with pumice impregnated with anhydrous copper sulphate (note below). The pure dry gas then passes through the weighed absorption-tube A, which is about four-fifths filled with soda-lime, the remaining portion, *a*, furthest removed from the incoming gas, being filled up with dry calcium chloride. Beyond the absorption-tube is a smaller U-tube containing soda-lime, which is weighed immediately before and after the experiment. This serves as a *guard* tube, and its weight should remain constant if the absorption-tube A is properly absorbing the whole of the carbon dioxide. After this guard tube is placed a

* The accuracy of the results obtained by this method depends very largely upon the slowness with which the carbon dioxide is disengaged. The method is more suitable for those carbonates which give up the whole of their carbon dioxide when acted upon by sulphuric acid ; in other words, carbonates of those metals which yield soluble sulphates. When hydrochloric or nitric acid is employed, an additional source of error is introduced by the volatilisation of small quantities of the acid during the process of expelling the carbon dioxide. This may, however, in a measure be prevented by attaching to the drying-tube *d* another small thin glass tube filled with particles of pumice which have been soaked in strong copper sulphate solution, and afterwards heated in an air-oven to 200°. The anhydrous copper sulphate absorbs hydrochloric acid as well as aqueous vapour.

U-tube containing sufficient strong sulphuric acid to cover the bend. This serves the double purpose of preventing the entrance of moisture to the guard tube, and also as an indicator of the rate at which the gas is passing through the tubes. The tube S, contain-

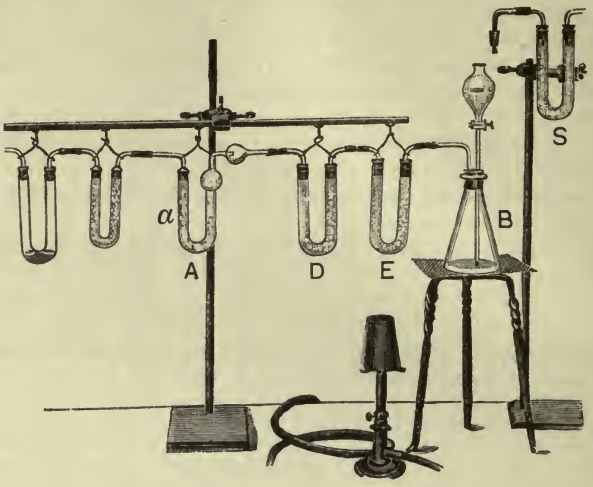

Fig. 56.

ing soda-lime, is for the purpose of removing carbon dioxide from the air which is drawn through the apparatus at the conclusion of the operation by means of the aspirator (see p. 204). This tube and the aspirator are not connected until the final stage of the process.

Estimation of CO_2 in Calcium Carbonate, $CaCO_3$.—Employ about 1 gram. The pure dry carbonate is weighed out into the flask B. The caoutchouc stopper carrying the funnel and exit-tube is inserted, and the funnel filled with dilute hydrochloric acid. The apparatus is then connected up as shown in the figure, the absorption-tube A having previously been weighed.* The acid is allowed slowly to enter the flask, the admission of the acid being regulated by the rate at which bubbles are seen to pass through the acid in the last tube; they should not escape faster than two

* It will be obvious that the apparatus must be perfectly free from leakage. Before being used, it may be tested by connecting a long vertical glass tube, dipping into a vessel of water, to the exit of the last U-tube, and then sucking air out of the apparatus, through the dropping-funnel, until a column of water has been drawn up the long tube. On closing the tap of the funnel, the water in the tube should remain stationary.

per second. When effervescence is at an end, the remainder of the acid is run in, the tap is left open, and the tube S is attached to the funnel. The aspirator is connected to the other end, and arranged to draw a *very slow* stream of air through the apparatus. A gentle heat is applied to the flask, and the temperature of the liquid kept for a short time just below the boiling-point. The aspiration should be continued for 15 to 20 minutes, to ensure the whole of the carbon dioxide being drawn out of the flask and absorbed in the soda-lime.

During this absorption the soda-lime becomes perceptibly warm, and loss would result from the escape of moisture from the material. This loss is prevented by the layer of calcium chloride contained in the tube.

When the process is concluded, the aspirator is stopped, and the absorption-tube A disconnected. The ends of the exit-tubes are at once closed with caps, and the tube carefully wiped and weighed. The caps are removed during the weighing.*

The increase in weight is the carbon dioxide expelled from the calcium carbonate employed.

Formula-weight of $CaCO_3$ = 100; theoretical percentage of CO_2 = 44.

Nitric Acid (NO_3).

Epitome of Process.—The nitrate is strongly heated with powdered silicon dioxide, whereby the whole of the N_2O_5 present in the nitrate is expelled, and the oxide of the metal remains associated with the silica.† The loss of weight represents N_2O_5, from which the proportion of NO_3 present can be calculated. Factor—

$$(N_2O_5)\ 108 : (2NO_3)\ 124 = 1 : 1{\cdot}148$$

Estimation of (NO_3) in Potassium Nitrate, KNO_3.—Employ 0·5 to 0·75 gram. From 2 to 3 grams of powdered quartz are placed in a platinum crucible; it is then strongly heated, and weighed after cooling. The dry powdered nitre (previously prepared by *just* melting the salt in a porcelain dish, pouring out the fluid into a clean warm porcelain dish, and afterwards powdering it) is introduced into the crucible, and the whole weighed again. The nitrate and the silica are intimately mixed by means

* At the conclusion of the determination, the various purifying tubes may remain connected together, the extreme exits being closed with caps; they will then be ready for use in a second experiment.

† A few metallic nitrates, when heated *alone*, give up the whole of their N_2O_5, and leave only a metallic oxide; but most nitrates, when thus heated, leave a residue of uncertain composition

of a clean stout piece of wire or a fine glass rod, and the mixture heated in the covered crucible for about 20 minutes to a red heat.* It is then allowed to cool in the desiccator, and weighed ; the heating being repeated until no further loss takes place.

Formula-weight of KNO_3 = 101. Theoretical percentage of (NO_3) = 61·38.

Phosphoric Acid (PO_4).

Epitome of Process.—The phosphoric acid is precipitated in the form of ammonium magnesium phosphate by means of "magnesia mixture" (as in the estimation of arsenic, p. 254). The dried precipitate is converted by heat into magnesium pyrophosphate, in which form it is weighed (see Estimation of magnesium, p. 233). Factor—

$$(Mg_2P_2O_7)\ 222 : (2PO_4)\ 190 = 1 : 0{\cdot}8558$$

Silicic Acid.

Epitome of Process.—The silicic acid is precipitated in the gelatinous state by means of hydrochloric acid. The mixture is evaporated to dryness, whereby the precipitated acid is converted into the anhydride (silicon dioxide), SiO_2. The silica so obtained is then filtered, washed, and dried, and weighed in that form.

Silicates which are decomposed by acids, are treated at once with hydrochloric acid ; the majority are converted by fusion with alkaline carbonates into silicates of the alkalies, which are afterwards precipitated by hydrochloric acid (see p. 285).

* In general analysis, where there is any likelihood of chlorides or sulphates being present, the temperature should not rise above that at which the crucible is just visibly red hot, or loss will result from the decomposition of these compounds. In such a case, the heating should be prolonged to at least half an hour.

SECTION IV.

Exercises in Gravimetric Analysis.

Introduction. **Sampling and Powdering.**—When the substance to be analysed is a metal or an alloy of homogenous composition, the portion taken for analysis may be obtained by boring into the mass with a steel drill in a lathe, carefully catching the borings upon a clean sheet of paper. If this plan is not practicable, the metal may be cut with a clean sharp file, and the filings used for the analysis. In this case, however, there is always risk of particles of iron from the file becoming mixed with the sample. These can be removed (unless the metal happens to be iron, or other metal attracted by the magnet) by means of a magnet. When the bar, ingot, or piece of metal is small, it may be broken or cut into small pieces. In the case of metals, it is not necessary that the portion taken for analysis should be in a state of very fine subdivision ; the fragments obtained by boring or even by breaking or cutting are sufficiently small, as metals for the most part are dissolved without much difficulty. Should the borings or filings contract any oil or grease during their production, this should be removed by washing them with either benzol or carbon disulphide.

Solid substances which are capable of being powdered, such as minerals, ores, slags, etc., must be reduced to as fine powder as possible, and a portion selected for analysis which represents a fair sample of the whole. A number of the selected lumps of the substance are first broken down into small fragments : in a wedgwood mortar, if the material is moderately soft ; in a steel mortar, if hard ; or they may be broken up by wrapping them in a clean cloth and striking them with a hammer upon an anvil. These fragments are then reduced to a coarse powder ; with hard substances, the operation being performed in a steel percussion mortar (A, Fig. 57). This consists of three parts : the foot or base, *a* ; a short steel tube, *b*, which fits into the cavity in the base ; and a steel rod or plunger,

c, which will just pass into the tube or cylinder. A larger percussion mortar is shown at B, Fig. 57, in which a massive block of steel takes the place of the parts *a* and *b*. The fragments, in small quantities at a time, are placed in the tube, and the plunger or pestle introduced. This is then sharply struck with a fairly heavy hammer several times, which crushes the material into coarse powder. When all the lumps chosen have been crushed in this way, the coarse powder is spread upon a sheet of paper and thoroughly mixed with a spatula or paper-knife. A small portion

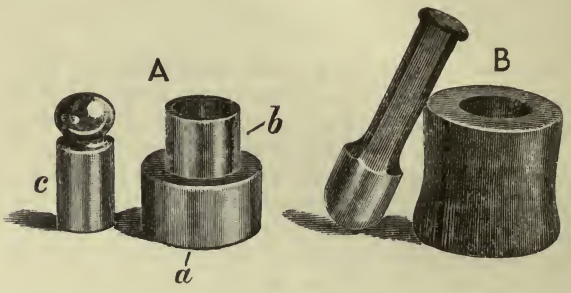

Fig. 57.

of this is then withdrawn, and reduced to the finest powder possible in an agate mortar. In carrying out this last operation, *small quantities at a time*, taken upon the end of a spatula, are put into the mortar, and powdered entirely by a *grinding* process, and not by using the pestle as a hammer, which would be liable to chip both the pestle and the mortar. The powder should then be passed through a fine sieve, which may be made by tying a piece of fine muslin tightly over the mouth of a broken beaker.* The portion which is retained upon the sieve should be returned to the mortar for further grinding, until the whole of it is reduced to a sufficiently fine powder to pass through.

* The little piece of muslin should be renewed before using the sieve for another mineral. If metal sieves are employed, the greatest care must be exercised to have them perfectly clean. Any traces of a former operation should be beaten and brushed out, and the sieve *rinsed* by sifting a small portion of the powder under examination through it, and rejecting the siftings. On no account should a sieve be wetted.

Analysis of Silver Coinage.

(*Alloy of Silver and Copper.*)

Epitome of Process.—The metal is dissolved in nitric acid, and the silver precipitated as silver chloride. This is separated, and weighed as such. The copper is precipitated from the filtrate in the form of copper hydroxide, which is converted by heat into copper oxide, and weighed in this form.

The silver coin (a new threepenny piece) is carefully weighed, and then dissolved in a little nitric acid in a small conical flask.* The acid, consisting of strong nitric acid, to which about half its volume of water has been added, is introduced by means of a small funnel, which should be allowed to remain in the mouth of the flask during the whole process, as it serves to prevent loss of the liquid by spirting. The solution is started by the application of a gentle heat, after which the action continues briskly until the metal is nearly all dissolved. A few more drops of acid may be added, if necessary, for the complete solution of the coin, but excess of acid is to be avoided.†

When the metal has entirely dissolved, the excess of acid is evaporated off by gently boiling the solution. The liquid is then diluted with water and transferred to a beaker, the flask and funnel being thoroughly rinsed once or twice with distilled water, so that the whole of the solution is transferred without loss.

From this solution the silver chloride is precipitated, and the silver estimated in the manner described on p. 238. The filtrate, together with the washings containing the copper, is heated to boiling, and the copper is estimated as described on p. 235.

A more expeditious way of carrying out the analysis is as follows. The metal is dissolved in a stoppered assay bottle, the operation being carried out exactly as described above, except that the bottle

* English silver coinage consists of 925 parts of Ag and 75 of Cu; 1 gram of the alloy therefore contains only 0·075 Cu. The weight of a threepenny piece is about 1·4 gram, which therefore contains 0·105 gram Cu, yielding 0·133 gram CuO. It is undesirable, therefore, to employ *less* than this weight of metal for the analysis. If a larger coin is used, it should be flattened out in a rolling machine, and the thin metal cut into fragments with a pair of scissors; or, in the absence of a roller, the coin may be broken by bending it backward and forward, holding it by means of two pairs of pliers. The requisite quantity is then weighed out.

† Old silver coins, especially the larger pieces, sometimes contain small quantities of gold, which will remain as a black residue after solution in nitric acid. Minute quantities may be neglected without affecting the result of the analysis.

requires to be heated with more care. It should be placed upon a piece of asbestos cloth, upon a hot iron plate (p. 223), or may be heated on a steam-bath. When the excess of acid has been evaporated, the liquid is diluted in the flask, and the silver chloride precipitated by the addition of hydrochloric acid. The stopper is then inserted, and the flask vigorously shaken for a few minutes. The precipitate is thus obtained in a condition which enables it to settle very rapidly, and the perfectly clear liquid is decanted off into a beaker as thoroughly as possible. The flask is then half filled with water, and the contents again thoroughly shaken, and after settling, the liquid is decanted. After two such washings the whole of the copper will have been washed out, and the solution containing the copper is boiled, and the copper estimated as already described.

The flask containing the silver chloride is then completely filled

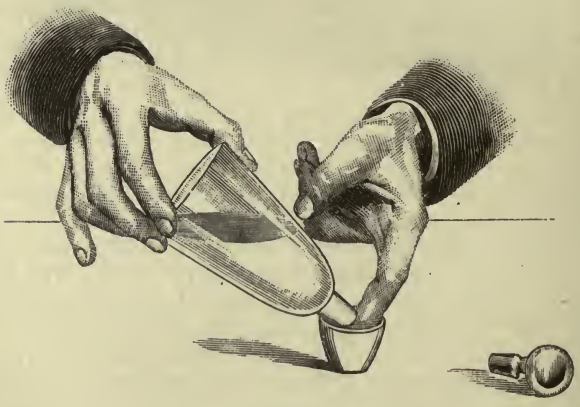

FIG. 58.

with water, the mouth is closed with the finger, and the vessel inverted into a weighed porcelain crucible filled with water, in the manner shown in Fig. 58. In this way the precipitate is transferred to the crucible, the whole of it being readily caused to fall down by gently tapping the flask. When the whole of the precipitate has settled to the bottom of the crucible, the flask is first gently raised to the level of the edge of the crucible, so as to allow one or two air-bubbles to enter and displace a little water, which will fill up and overflow the crucible, and then it is *quickly* drawn away sideways

(being held in the position shown in Fig. 59) and allowed to empty.* The water in the crucible is then carefully decanted as much as possible, and the crucible placed in the steam-oven to dry. When dry, the crucible may be gently heated until the silver

Fig. 59.

chloride just begins to melt; and after cooling in the desiccator, it is weighed.

Usually unglazed crucibles are employed for this operation. The precipitate dries more quickly in such a crucible, and the chloride is not heated after it is removed from the steam-oven.

Analysis of Common Solder.

(*Alloy of tin and lead.*)

Epitome of Process.—The alloy is acted upon by strong nitric acid, which converts the tin into stannic oxide, SnO_2, in which form the tin is estimated. The lead passes into solution as lead nitrate, from which it is precipitated in the form of lead sulphate, $PbSO_4$, by sulphuric acid, and weighed as such. Employ about 0·5 gram.†

* This operation is quite easily accomplished without disturbing the precipitate in the crucible. The student should perform the experiment of filling an empty flask with water, inverting it in a crucible, and then withdrawing the flask as here directed. He will find that there is no difficulty in drawing the flask aside without letting an air-bubble pass up, which would of course cause a disturbance in the crucible, and throw out any precipitate it contained. As a precaution, the crucible may be placed in a shallow glass basin, so that, should any of the precipitate be accidentally thrown out, it will not be lost.

† Common solder consists of about equal parts of tin and lead, but as there are varieties of solder in commerce containing these metals in different proportions, a duplicate estimation of one at least of the constituents should be made as a check.

Tin.—The alloy is weighed out into a porcelain dish, and dissolved in a small quantity of moderately strong nitric acid, the dish being covered with a clock-glass. When all action has ceased, the cover is rinsed into the dish, and the mixture evaporated nearly to dryness upon a steam-bath. Water is added, and the residue of stannic oxide is transferred to a filter and washed.

After the stannic oxide has been dried in the steam-oven, it is transferred to a porcelain crucible, being detached as completely as possible from the paper. The filter is incinerated in a platinum coil, care being taken to fold the soiled portion of the paper into the interior of the roll. The ash is moistened with a drop of nitric acid, and the crucible with its contents heated, first gently to expel the acid, and afterwards to a red heat. It is then cooled in the desiccator and weighed.

Lead.—The filtrate containing the lead is precipitated with sulphuric acid, and the lead estimated as lead sulphate (see p. 242).

Analysis of German Silver.

(*Alloy of copper, zinc, and nickel, with traces of tin and iron.*)

Epitome of Process.—The alloy is dissolved in nitric acid, and the insoluble residue of stannic oxide separated and weighed.

The copper is next precipitated as sulphide by means of sulphuretted hydrogen, and estimated as Cu_2S.

The filtrate containing the zinc, nickel (and iron), is boiled to expel sulphuretted hydrogen, and a few drops of nitric acid added to oxidise the iron, which is then precipitated as hydrated oxide by means of ammonia, and estimated as Fe_2O_3.

The zinc is next precipitated as sulphide by means of hydrogen sodium sulphide, HNaS, in the presence of potassium cyanide, and estimated as ZnS.*

The filtrate is acidified with nitric acid and boiled to expel the hydrogen cyanide, after which the nickel is precipitated as hydroxide by means of potassium hydroxide, and estimated as NiO.

Tin.—About 1 gram of German silver wire or borings is dissolved in strong nitric acid, and the mixture evaporated almost to dryness upon a steam-bath. The residue is dissolved in water, and the solution filtered to remove the traces of stannic oxide. After being thoroughly washed, the filter is neglected, as the estimation of the tin will be made in a separate larger quantity of the alloy.†

* For alternative methods of separating zinc and nickel, see p. 272.

† In the case of alloys in which tin forms one of the *intended* constituents, as in the various bronzes, this residue should be treated as described on p. 272. Approximately, the composition of German silver is—Cu, 55 to 60 parts; Zn, 22 to 27; and Ni, 15 to 20. In many samples the amount of tin is too small to be determined. A qualitative analysis should be first made, in order to ascertain whether the sample contains any tin and iron.

Copper.—About 30 c.c. of strong hydrochloric acid are added to the filtrate, and the solution considerably diluted with hot water. It is then heated to boiling, and a stream of sulphuretted hydrogen passed through for about 20 minutes. The liquid is then filtered quickly, and the precipitate washed with warm water containing sulphuretted hydrogen.

The copper sulphide so precipitated is liable to carry down with it small quantities of the zinc, also as sulphide; it is necessary, therefore, to dissolve it and re-precipitate the copper. For this purpose the precipitate is transferred to a porcelain dish, and dissolved in strong nitric acid previously mixed with about half its volume of saturated bromine water, and the solution evaporated to dryness upon a steam-bath.

The residue is dissolved in about 30 c.c. of strong hydrochloric acid, and the solution rinsed into a beaker and considerably diluted. It is once more boiled, and a stream of sulphuretted hydrogen passed through it. The precipitated copper sulphide is filtered and washed as before, with warm water containing sulphuretted hydrogen, the washing being continued until the wash-water is free from hydrochloric acid. (Indicated by silver nitrate, after boiling off the sulphuretted hydrogen.)

The precipitate is dried, and treated as described on p. 237.

Iron.—The filtrates and washings from both precipitations of the copper are mixed together and briskly boiled in a covered beaker, in order to expel the sulphuretted hydrogen, after which the liquid is evaporated until the volume is reduced to about 200 c.c.

Two or three drops of nitric acid are introduced in order to oxidise the iron, after which a moderate quantity of ammonium chloride is added, and then a slight excess of ammonia. The precipitated ferric hydroxide is filtered and washed with a little hot water. It is then dissolved in a little hot hydrochloric acid, and re-precipitated with ammonia, and again filtered and thoroughly washed. The precipitate is neglected, as the iron, if only present in traces, is estimated in a separate larger quantity of the alloy.

Zinc.—The two filtrates from the iron precipitations are mixed and boiled until the steam no longer smells of ammonia, and the liquid concentrated somewhat by evaporation. A freshly made concentrated solution of potassium cyanide is then added, until the yellowish colour produced by the soluble double cyanide of potassium and nickel becomes no deeper by the further addition of the reagent. Hydrogen sodium sulphide, HNaS, is now added, and the liquid heated to boiling.

The precipitation of the zinc sulphide, which begins almost directly the liquid is heated, is complete after the mixture has boiled for a few minutes. The mixture is filtered, and the precipitate washed with hot water, and estimated as zinc sulphide, as described on p. 244.

Nickel.—The solution containing the double cyanide of potassium and nickel, with excess of sodium sulphide, is evaporated down to a moderately small bulk,* and strong nitric acid cautiously added drop by drop until there is no further effervescence. Both the cyanides and the sodium sulphide are thereby decomposed; the former with evolution of hydrocyanic acid (hence the operation should be conducted in a draught-cupboard), while from the latter sulphur is precipitated, which is at once attacked by the acid, with the evolution of brown fumes. The mixture is boiled until the precipitated sulphur is entirely oxidised to sulphuric acid, after which potassium hydroxide is added until the precipitation of the hydrated oxide of nickel is complete.

The precipitate is then treated as described on p. 247.

Separate Estimation of Tin and Iron.—For this purpose, about 5 grams of the alloy are weighed out and dissolved in nitric acid, and the solution evaporated and treated as described above. The residue of stannic oxide is filtered off, and estimated as on p. 270.

The filtrate is treated as described above for the separation of copper; in this case, however, one precipitation only is necessary. The precipitate, after being thoroughly washed, is neglected. The filtrate and washings are together boiled to expel the sulphuretted hydrogen, and the iron precipitated as hydrated oxide by means of ammonia. The precipitate is treated as described on p. 230.

Alternative methods for the Separation of Zinc and Nickel. (1) *Precipitation of Zinc Sulphide from Acetic Acid solution.*—After the removal of the tin, copper, and iron as described above, the liquid containing the zinc and nickel is acidified with hydrochloric acid, and evaporated down until its volume is reduced to about 150 c.c. Sodium carbonate solution is then added until a *slight* precipitate persists, after which acetic acid is added until the precipitate is redissolved.† Sulphuretted hydrogen is then

* If the precipitation of the zinc has been made in too dilute a solution, a further slight separation of ZnS may take place during this concentration. In that case the liquid must be filtered, and the precipitate either added to the main portion, or else separately weighed and the result added.

† Or the precipitate may be redissolved by adding hydrochloric acid drop by drop, and then removing the free acid by the addition of a few drops of a

passed through the mixture, when the white zinc sulphide is alone precipitated. When precipitation is complete, the liquid may be gently warmed and filtered. The precipitate is then treated as already described. The filtrate is heated to expel sulphuretted hydrogen, and the nickel precipitated as hydrated oxide by means of potassium hydroxide, and the process carried on as above.

(2) *Precipitation of Zinc Sulphide from a Succinic Acid solution.* —In order to carry out the separation by this method, the iron must previously have been removed, not by means of ammonia, but with sodium acetate.*

The solution containing the iron, zinc, and nickel (after separation of the copper as described on p. 271) is boiled to expel sulphuretted hydrogen, and oxidised with nitric acid as before. It is then made nearly neutral with sodium carbonate ; sodium acetate is added, and the liquid boiled until the iron is completely precipitated as basic acetate (see footnote, p. 70). The precipitate is filtered off and thoroughly washed, after which it may be neglected.†

The filtrate and washings are together boiled with hydrochloric acid until the acetates are entirely destroyed and the steam no longer smells of acetic acid, after which the zinc and nickel are together precipitated as carbonates by the addition of sodium carbonate. The liquid is filtered and the precipitate washed, after which it is dissolved upon the filter by slowly pouring over it a hot strong solution of succinic acid. The funnel should be kept covered with a clock-glass to avoid loss due to effervescence. When the precipitate is completely dissolved, and the filter thoroughly washed with hot water, sulphuretted hydrogen is passed through the liquid while still hot, until the zinc is completely precipitated. The zinc sulphide thrown down under these circumstances settles very readily. The sulphide is filtered off, and treated as already described.

The solution is boiled to expel sulphuretted hydrogen, and the nickel precipitated as in the former methods by means of potassium hydroxide.

solution of ammonium acetate, which, by double decomposition, forms ammonium chloride and acetic acid. More than quite a small quantity of the acetate must be carefully avoided, or else the nickel will be partially precipitated by the sulphuretted hydrogen.

* The reason for this is, that the precipitation of zinc as carbonate, by means of sodium carbonate, is not complete in the presence of ammoniacal salts.

† In cases where iron is present in sufficient quantity to be estimated at this stage, this precipitate of basic acetate must be dissolved in hydrochloric acid ; and, after boiling, the iron is precipitated as hydrated oxide by means of ammonia, and treated as already described.

Analysis of Bronze Coinage.

(*Alloy of copper, tin, and zinc, with traces of lead.*)

Epitome of Process.—The alloy is dissolved in nitric acid, and the solution evaporated to dryness. The residue is extracted with water, and the insoluble stannic oxide dried and weighed.

Sulphuric acid is added to the filtrate, which is then evaporated to a small bulk, and the lead sulphate separated and weighed.

The solution is diluted with water to a definite volume, and a small measured proportion of it taken in which to estimate the copper ; the copper in this separate portion being precipitated as cuprous thiocyanate.

In the main portion of the solution, the copper is separated from the zinc by means of sulphuretted hydrogen (the precipitated copper sulphide being neglected), and the zinc is estimated in the filtrate.

Tin.—A clean new halfpenny * is weighed, and dissolved in strong nitric acid in a covered beaker. The solution is then transferred to a porcelain dish, and evaporated to dryness on a steam-bath. The residue is treated with water, and the insoluble stannic oxide filtered and thoroughly washed. It is dried, and treated as described on p. 270.

The stannic oxide, however, is liable to retain traces of the copper ; it should therefore be submitted to the following treatment after it has been weighed : A small quantity of sulphur (about equal to the weight of the stannic oxide) and the same amount of sodium carbonate are mixed together in the crucible, which with its cover is then gently heated until the mass fuses and the excess of sulphur is expelled. When cold, the mass is boiled with water, which dissolves the sodium thiostannate, and if any copper were present, it remains as a black residue of copper sulphide. It is filtered, thoroughly washed, and dissolved in nitric acid. The copper is then precipitated with potassium hydroxide, and estimated as CuO, the weight being deducted from the weight of the stannic oxide.

Lead.†—The filtrate from the stannic oxide is acidulated by the addition of about 10 c.c. of strong sulphuric acid (free from

* English bronze coinage consists roughly of Cu 95, tin 4, zinc 1. A halfpenny weighs about 5½ grams. This weight, while affording enough material in which to estimate the zinc, is much more than is necessary for the copper determination, hence the latter is estimated in a small portion of the solution.

† It is seldom that bronze coinage contains more than from 0·05 to 0·1 per cent. of lead. In 5 grams of the alloy, 0·1 per cent. of lead would represent 0·005 gram of the metal, or 0·007 gram of $PbSO_4$, a quantity far too small to be estimated, and scarcely a perceptible turbidity will be seen. This step in the analysis may therefore be omitted without any appreciable influence upon the result. It is given in the description because other varieties of bronze contain appreciable quantities of lead, which would be separated as here explained.

lead),* and evaporated until the liquid gives off vapours of sulphuric acid freely. It is then allowed to cool, diluted with water, and filtered. The precipitated lead sulphate is washed with dilute sulphuric acid (in which it is far less soluble than in water) until the washings are free from copper, when the vessel containing the filtrate is removed, and the filter is washed free from sulphuric acid by means of methylated spirit. (If the acid were not thus washed out, the paper would become charred, and impossible to manipulate, when dried in the oven. The alcoholic washings are thrown away.)

The lead sulphate is dried, and treated as described on p. 242.

Copper.—The filtrate containing the copper and zinc is diluted with water in a half-litre flask until its volume is 500 c.c. By means of a graduated pipette, 50 c.c. of this solution are withdrawn and transferred to a beaker, and the copper precipitated as cuprous thiocyanate by means of ammonium thiocyanate in the manner described on p. 237.

The amount of copper present in this 50 c.c. of the solution will obviously be one-tenth of that present in the entire volume, and if any copper was recovered from the stannic oxide in the first separation, this must be added on in order to obtain the total weight of copper in the quantity of alloy taken for the analysis.

Zinc.—The main portion of the solution (450 c.c.) containing the copper and zinc, is acidified by adding about 50 c.c. strong hydrochloric acid, and diluted by the addition of 300 c.c. of hot water. The mixture is heated to boiling, and the copper completely precipitated by means of sulphuretted hydrogen.

The precipitated copper sulphide is treated as described on p. 271, the double precipitation being even more necessary in this example, where the proportion of copper to that of zinc is so large. The final precipitate of copper sulphide is here neglected, the copper having been already estimated.

The solutions containing the zinc are then evaporated down to moderate bulk, and the zinc estimated as on p. 244.

The weight of the zinc so obtained will be nine-tenths of that present in the amount of alloy employed for the analysis.

* Ordinary sulphuric acid contains considerable quantities of lead. If pure acid is not available, acid must be used which has been previously largely diluted and allowed to settle, and a proportionately larger volume will be necessary.

Analysis of Dolomite.

(*Magnesium and calcium carbonate, containing usually small quantities of iron, aluminium, and insoluble silicious matter*).*

Epitome of Process.—The mineral is dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue is treated with hydrochloric acid and water, and the insoluble portion, consisting of silica and silicates, is filtered off, washed, and dried.

The iron and alumina are precipitated together as hydroxides, by the addition of ammonium chloride and ammonia to the filtrate. The precipitate is dried, and weighed as oxides of iron and aluminium.

The filtrate is boiled, and the calcium precipitated as oxalate by means of ammonium oxalate, the precipitation being repeated to ensure complete separation of the magnesium. The precipitate is dried and converted by heat into calcium oxide, and weighed.

The filtrate from the calcium is evaporated to dryness, and heated to expel excess of ammonium salts. The residue is dissolved in hydrochloric acid, diluted with water, and the magnesium precipitated as ammonium magnesium phosphate by the addition of ammonia and sodium phosphate.

The carbon dioxide is estimated in a separate portion of the mineral by the method described on p. 259.

Silicious Matter.—About 2 grams of the finely powdered mineral (which has been previously dried in an air-oven at a temperature of about 200° †) is weighed out into a porcelain dish covered with a clock-glass, and dissolved by the cautious addition of dilute hydrochloric acid. As soon as action ceases, the cover is rinsed into the dish, a few drops of strong nitric acid added, and the mixture evaporated to complete dryness upon a steam-bath. The residue is then treated with a little strong hydrochloric acid, and gently warmed. Water is then added, and the insoluble residue of silica and insoluble silicates is transferred to a filter, where it is washed free from hydrochloric acid. It is then dried in the steam-oven.

The dried filter with the residue is folded up and placed in a platinum crucible, where it is strongly heated until the paper is completely incinerated.‡ The crucible, after cooling in the desiccator, is weighed.

* Occasionally manganese is met with in varieties of dolomite, but usually only in traces, which may be neglected.

† The amount of moisture present in dolomite is usually very small. If desired, it may be estimated by heating about 10 grams of the powder to 200° in the air-oven.

‡ Usually the amount of silicious matter does not exceed about two per cent. In cases where there is much insoluble residue, it should be detached from the paper, and the latter incinerated apart in a platinum coil.

Aluminium and Iron.*—A considerable quantity of ammonium chloride is added to the filtrate (see note on p. 224), and the solution gently warmed; ammonia is then added, the least possible excess being used, and the mixture boiled. The precipitated hydroxides of aluminium and iron are then filtered and washed; the precipitate is dissolved upon the filter by pouring a little warm dilute hydrochloric acid upon it (the liquid being received in a separate beaker), and the acid solution thoroughly washed out of the paper.

The aluminium and iron are then re-precipitated from this solution by the addition of a slight excess of ammonia; the precipitate is filtered and washed until the washings are free from chlorides, and then dried in the steam-oven. The dry precipitate, if small in amount, is heated with the paper in a platinum crucible; if the amount is considerable, it is detached from the filter, and the latter is separately incinerated in a platinum coil. The precipitate, after being heated, consists of a mixture of Al_2O_3 and Fe_2O_3; it is weighed and calculated as such.†

Calcium.—The mixed filtrates and washings from the double precipitation of iron and aluminium are heated to boiling, and the calcium precipitated by means of ammonium oxalate, as described on p. 231. *Excess* of the reagent must in this case be used, since, in the presence of magnesium chloride, the precipitation of calcium oxalate is not complete unless excess of ammonium oxalate is present. The reagent may be added in a solid state (instead of a hot strong solution, as directed on p. 231), three or four grams of the powdered salt being introduced into the boiling liquid, and the mixture stirred for a few minutes.

The precipitated calcium oxalate carries down with it small quantities of magnesium oxalate; it is therefore necessary to repeat the precipitation. For this purpose the precipitate is allowed to settle, and the clear liquid decanted off through a filter without disturbing the precipitate; the latter is twice washed by decantation, each time being allowed to thoroughly settle, so that the least possible trace of it only is transferred to the filter. It is then dissolved in the beaker by the addition of a little warm dilute hydrochloric acid, and reprecipitated by the addition of ammonia

* Should the ore contain more than very small quantities of manganese (which, however, is not usually the case), the iron and aluminium must be separated as basic acetates, as described for iron on p. 282.

† If the quantity of aluminium and iron is considerable, and it is desired to determine the metals separately, the precipitate may be treated as described on p. 278.

in slight excess, and a few drops of ammonium oxalate solution.* This precipitate is allowed to settle, and transferred to the same filter employed in the first operation; it is washed and dried, and treated as described on p. 233.

Magnesium.—The filtrates and washings from the calcium precipitate are evaporated to dryness in a porcelain dish. The evaporation may be conducted at first over a gas-burner, provided the liquid is not permitted to boil; but as the liquid begins to deposit salts, the further heating must be done upon a steam-bath.† The dish with the dry residue is heated over a ring gas-burner, at first very cautiously, until the ammonium salts are expelled.

When the dish is cold, the residue is dissolved by the addition of a little strong hydrochloric acid, and gently warming the mixture. The solution is diluted with water, and if not perfectly clear it is filtered, the residue in this case being neglected.

Ammonia in slight excess is added (no precipitate should form, as the ammonium chloride produced by the neutralisation of the solution will be sufficient to prevent the precipitation of the magnesium hydroxide), and the magnesium then precipitated as ammonium magnesium phosphate by the addition of hydrogen disodium phosphate. The precipitation and the treatment of the precipitate are described on p. 233.

NOTE.—Iron and aluminium are associated together in varying proportions in a great number of common minerals which come under analysis, such as iron ores, clays, felspar, and other silicates, as well as slags and other artificial products. They may be separated and determined by the following methods :—

Separation of Iron and Aluminium.—(1) The precipitated hydroxides are dissolved upon the filter in a little warm hydrochloric acid, and the solution poured into a strong solution of sodium or potassium hydroxide (free from alumina) contained in a dish (preferably of either silver, platinum, or nickel, although porcelain may be used in the absence of these). The mixture is then boiled for two or three minutes. The iron is precipitated as ferric hydroxide, while the aluminium passes into solution as sodium aluminate. The precipitate is filtered off, washed with

* Or the second precipitation may be conducted as in the case of the iron and aluminium; *i.e.* the precipitate may be washed upon the filter, and dissolved by the addition of acid to it while in the funnel.

† Solutions of ammoniacal salts are very apt, during evaporation, to be drawn up through the crust of deposit which forms round the edge of the liquid, so that the salt is continually deposited higher and higher upon the sides of the dish, until eventually it creeps over the edge. To prevent this, the finger, *slightly* greased with vaseline, should be drawn round the inside edge of the dish at the beginning of the operation.

water, then redissolved in hydrochloric acid and reprecipitated with ammonia.* The ferric hydroxide is again filtered, washed and dried in the usual way, and weighed in the form of sesquioxide (p. 230). The two filtrates are together acidified with strong hydrochloric acid, and the aluminium precipitated as hydroxide by the addition of ammonia in slight excess. The precipitate is washed and dried, and weighed in the form of sesquioxide, as described on p. 225.

(2) When pure caustic soda or potash (*i.e.* free from alumina) is not at hand, the process may be modified in the following way, and the aluminium estimated by *difference*. The precipitated hydroxides of the two metals are dried and weighed together as sesquioxides. A quantity of powdered sodium peroxide † is then mixed with the precipitate in the crucible (platinum), and the mixture fused. The fused mass when cold is cautiously treated with water in a beaker (as the aluminium is not to be *directly* determined, glass vessels may be used), when the sodium aluminate will dissolve, leaving the ferric oxide. This is then filtered and washed, the filtrate being rejected. The precipitate is then dissolved in hydrochloric acid, reprecipitated with ammonia, and determined in the usual way. The weight of the ferric oxide thus obtained, deducted from the weight of the two oxides together, gives the weight of the aluminium sesquioxide.

(3) The amount of iron may be determined, and the aluminium estimated by difference, by the use of volumetric methods for estimating iron. The mixed oxides are weighed as in the above process; they are then dissolved in hydrochloric acid, and the iron determined volumetrically,‡ without separating the aluminium. The amount of sesquioxide of iron corresponding to the iron thus determined, when deducted from the original weight of the mixed oxides, gives the weight of the sesquioxide of aluminium.

Analysis of Zinc-blende.

(*Zinc sulphide, liable to contain zinc carbonate; and lead, copper, cadmium, iron, and manganese, as sulphides or in other forms. A previous qualitative analysis must be made.*)

Epitome of Process. — The ore is decomposed by strong hydrochloric and nitric acids. Any lead present is converted into sulphate and weighed along with the silicious matter, or gangue, from which it is afterwards separated by solution in ammonium acetate.

Copper and cadmium, if present, are precipitated together from the solution as sulphides, which are afterwards separated by dissolving the latter in dilute sulphuric acid.

* This second precipitation is necessary in order to remove the potash which is retained by the ferric hydroxide.

† Caustic soda may be substituted, although the peroxide is preferable.

‡ See Volumetric methods.

Iron is next separated in the form of the basic acetate,* the sulphates present having been first converted into chlorides by means of barium chloride.

The manganese is precipitated as hydrated peroxide by means of chlorine or bromine; and, lastly, the zinc is determined by precipitation as zinc sulphide.

The sulphur in the ore is estimated in a separate portion by oxidation into sulphuric acid, and subsequent precipitation as barium sulphate.

If the ore contains any calamine (zinc carbonate), the carbon dioxide is determined in a separate portion by the method described on p. 259.

Sulphur.—About 1 gram of the ore (which has been reduced to as fine a powder as possible, and dried in a steam-oven) is weighed into a platinum crucible, and then mixed thoroughly with five or six times its weight of powdered sodium peroxide, the mixing being done by means of a thin glass rod or stout platinum wire. The covered crucible is then cautiously heated by means of a small flame placed some little distance below it. Considerable action takes place, the contents of the crucible undergoing incipient deflagration, and becoming liquid. It is kept in a state of fusion for a few minutes, and allowed to cool. The crucible is then placed upon its side in a beaker, along with the lid, and water cautiously added, the beaker being covered to prevent loss during the effervescence which takes place owing to the escape of oxygen from the excess of peroxide.

When the solid is detached from the crucible, the latter is lifted out with a clean pair of tongs and rinsed with water; the lid is removed and washed into the beaker in the same way. The solution is then acidified with hydrochloric acid, filtered if necessary, and the sulphuric acid precipitated as barium sulphate by means of barium chloride in the usual manner (p. 258).† From

* If there is no manganese in the ore, the iron and zinc may be separated by precipitation of the former by means of ammonia, according to the method described on p. 277.

† Instead of employing sodium peroxide as the oxidising agent, strong nitric acid may be used. For this purpose the powdered ore is digested in a flask at a gentle heat (see Fig. 39) with strong nitric acid, to which, as the operation proceeds, a little hydrochloric acid or a few crystals of potassium chlorate are added; or fuming nitric acid (sp. gr. 1·5) may be employed alone. When the action is complete, and the whole of the sulphur (which at first often separates out and floats about in liquid drops) is oxidised into sulphuric acid, a little pure sodium chloride is added. This converts the sulphuric acid into sodium sulphate, and so prevents its volatilisation during the subsequent process of evaporation. The solution is then evaporated in a porcelain dish upon a steam-bath. When nearly dry, a little strong hydrochloric acid is added, and the mixture evaporated to dryness. The residue

the weight of barium sulphate obtained, the proportion of sulphur is calculated. Factor—

$$(BaSO_4)\ 233 : (S)\ 32 = 1 : 0{\cdot}1375$$

Silicious Matter and Lead.—About 2 grams of the dry and finely powdered ore are weighed out into a beaker, and 20 to 25 c.c. of strong hydrochloric acid added. The beaker should be immediately covered, since if any carbonate is present there will be effervescence. The mixture is then gently boiled until sulphuretted hydrogen is no longer given off, when about 20 c.c. of strong nitric acid are added, and the heating continued until the decomposition of the ore is complete. The contents of the beaker are then rinsed into a porcelain dish and evaporated to dryness upon a steam-bath, after which the dish with the dry residue is placed in an air-oven and heated to about 160° to render the silica insoluble. The residue is next moistened with strong hydrochloric acid, and about 5 c.c. of strong sulphuric acid, previously diluted with twice its own volume of water, added. The mixture is then cautiously heated on a sand-bath until fumes of sulphuric acid are given off, by which time all the nitrates and chlorides will have been converted into sulphates, and their acids expelled. The dish is then allowed to cool, water is added, and the mixture filtered. The residue, consisting of silicious matter and lead sulphate, is washed with water acidulated with sulphuric acid, the filtrate and washings being set aside for the estimation of the remaining constituents.

In order that the residue may be dried without the paper becoming charred, the dilute acid is first washed out of it by means of alcohol, the washings being neglected. The dried residue is then transferred to a porcelain crucible, and the incineration of the paper conducted as described in the estimation of lead as sulphate (p. 242). The weight obtained is that of the silicious matter and the

is again treated with hydrochloric acid, and once more taken down to dryness in order to completely expel the nitric acid. It is finally dissolved in water with a little hydrochloric acid, filtered, and diluted to about 100 c.c. The sulphuric acid is then precipitated as barium sulphate in the usual way. The residue may contain lead sulphate along with the gangue. If, therefore, lead is present in the ore, this residue must be treated as described above, and the amount of sulphur which has been thus carried down in combination with the lead must be added to the total weight of sulphur.

The sulphur in natural sulphides is usually estimated either by this process or by oxidation with sodium peroxide, the latter being the quicker process. Oxidation of the sulphur may, however, be effected by other methods, such as by fusion with a mixture of sodium carbonate and potassium nitrate, or by digesting the ore in a strong solution of caustic potash, and passing a stream of chlorine through the mixture.

lead sulphate together. The contents of the crucible are then transferred to a small beaker, and gently boiled with a solution of ammonium acetate and ammonia ; it is allowed to settle, and the liquid decanted through a small filter. It is treated to successive extractions with fresh portions of the ammonium acetate solution until the whole of the lead sulphate is dissolved out, the completion of the process being ascertained by testing a drop of the filtrate with ammonium sulphide.

The residue is then dried, and the paper incinerated either in the crucible along with the residue, or upon a platinum spiral. The result gives the weight of the silicious matter alone, the difference between this and the former weighing being the proportion of lead sulphate, from which the percentage of lead is deduced by the factor on p. 242.

Copper and Cadmium.—To the solution containing the remaining metals,* 10 to 15 c.c. of strong hydrochloric acid are added, and sulphuretted hydrogen is passed through until precipitation is complete. If cadmium is absent, the precipitate is treated as described on p. 236 (Estimation of copper as sulphide). If, however, the ore contains cadmium, the precipitate of the mixed sulphides, after being thoroughly washed, is boiled with dilute sulphuric acid (strong acid 1 part, water 5 parts). It is then filtered, and the insoluble copper sulphide washed and dried, and treated as described on p. 237. The filtrate and washings containing the cadmium are neutralised with ammonia, one or two drops of hydrochloric acid added, and the cadmium precipitated as sulphide by means of sulphuretted hydrogen. The precipitate is treated as described on p. 257.

Iron.†—The filtrate from the first precipitation with sulphuretted hydrogen is boiled until the gas is entirely expelled, and a few drops of nitric acid are added in order to re-oxidise the iron. Barium chloride is then added so long as a precipitate is produced, and the barium sulphate filtered off and washed. The precipitate is neglected. In this way the sulphates present are converted into chlorides. The solution is then nearly neutralised with ammonium carbonate, by adding the reagent cautiously until a slight precipitate persists, and then adding hydrochloric acid drop by drop with

* This solution should not be less than about 150 c.c. in volume. If the washings from the insoluble residue do not bring it up to this, it must be diluted with water.

† If the ore contains no manganese, the iron may be precipitated as hydroxide by means of ammonia (as described on p. 230) after the sulphuretted hydrogen has been boiled off and the iron re-oxidised with nitric acid.

constant stirring, until the precipitate is almost completely redissolved, leaving the solution just slightly turbid.* A strong solution of ammonium acetate, acidified with acetic acid, is then added, and the solution, which assumes a red colour, is boiled for a few minutes, when the basic ferric acetate separates as a voluminous reddish precipitate. This is allowed to settle, and the colourless liquid decanted through a filter, to which the precipitate is then transferred and washed with hot water.† The precipitate is then dissolved in hydrochloric acid, the solution again neutralised with ammonium carbonate, and the iron reprecipitated with ammonium acetate, filtered, and washed. The filtrate and washings from this second precipitation (which is necessary for the complete separation of the manganese) are added to those from the first operation. The precipitate is dried, and the filter incinerated with the precipitate, which is then strongly heated in the crucible until it is completely converted into the sesquioxide, Fe_2O_3, in which form it is weighed.‡

Manganese.§—The filtrates from the double precipitation of the iron are together evaporated down until the volume is reduced to about 100 c.c. Ammonia is then added until the solution is strongly alkaline, and the mixture heated nearly to boiling. Saturated bromine water is then added to the boiling liquid until the precipitation of the hydrated peroxide is complete, and the solution is distinctly yellow. The precipitate is then filtered off, and washed and dried. The dried precipitate, after the incineration of the paper, is strongly heated in the crucible until it is completely converted into the tetroxide, Mn_3O_4, in which form it is weighed.‖

Zinc.—The alkaline filtrate from the manganese separation is saturated with sulphuretted hydrogen (or colourless ammonium sulphide may be added), and the zinc estimated as sulphide, as

* The least excess of hydrochloric acid must be avoided.

† This precipitate is difficult to wash, especially if it has been boiled too long, when it is apt to become slimy. In cases where there is a considerable quantity of the precipitate, the funnel should be kept hot by one of the arrangements described on p. 210.

‡ When sodium acetate is used for the precipitation instead of the ammonium salt, the basic ferric acetate must be dissolved in hydrochloric acid, and the iron precipitated as hydroxide by means of ammonia.

§ The manganese cannot satisfactorily be precipitated as the carbonate from a solution containing considerable quantities of acetates.

‖ If sodium acetate has been employed in the previous separation of the iron instead of ammonium acetate, the process for the estimation of the manganese must be modified, since the hydrated peroxide retains portions of the alkali which are not removed by washing, and being non-volatile they remain behind with the manganese in the crucible. In this case the hydrated peroxide must be dissolved in hydrochloric acid, and the manganese precipitated as carbonate by means of sodium carbonate (p. 245).

described on p. 244. Or the precipitated zinc sulphide, after being filtered off, may be dissolved in dilute hydrochloric acid, the solution boiled, and the zinc precipitated as carbonate by means of sodium carbonate, and estimated in the form of zinc oxide according to the method given on p. 243, or by the volumetric method described on p. 371.

NOTE.—The analyses of other natural sulphides, such as copper-pyrites, iron-pyrites, galena, etc., are conducted on the same general lines as are described above, except that certain necessary modifications have to be introduced depending upon the particular metals present in the ore. Thus, copper and iron pyrites are liable to contain arsenic, or arsenic and antimony. These are precipitated as sulphides along with the copper, and afterwards separated from the copper sulphide by solution in sodium sulphide.* From this solution the sulphides of arsenic and antimony are reprecipitated by acidifying with hydrochloric acid and passing sulphuretted hydrogen, and the elements separated by the following method.

Separation of Arsenic and Antimony.—The two sulphides are dissolved in strong hydrochloric acid, with the addition of crystals of potassium chlorate; tartaric acid and ammonium chloride are added in considerable quantity, then an excess of ammonia. (The addition of ammonia should cause no precipitation; should a precipitate form, it is due to insufficient tartaric acid and ammonium chloride, and more must be added.) The arsenic is then precipitated as ammonium magnesium arsenate † by means of "magnesia mixture," and weighed as magnesium pyro-arsenate, as described on p. 254. The antimony contained in the solution is precipitated as antimonious sulphide by means of sulphuretted hydrogen, and finally weighed in the form of the tetroxide, as described on p. 256.

Galena often contains silver besides other metals. The ore in this case is decomposed by strong nitric acid (sp. gr. 1·5), the lead converted into sulphate by means of sulphuric acid, and the lead sulphate and silicious matter separated together. The silver is then precipitated as silver chloride by means of hydrochloric acid, and estimated as directed on p. 238, while the remaining metals, such as copper, antimony, iron, zinc, which are liable to be present, are separated as explained above.

* Sodium sulphide is prepared by saturating a solution of sodium hydroxide with sulphuretted hydrogen, and then adding fresh sodium hydroxide solution until the mixture ceases to smell of the gas (see "Reagents," Appendix).

† Precipitated under these conditions, especially if the quantity of arsenic is large, the ammonium magnesium arsenate is liable to contain a little basic magnesium tartrate. It is desirable, therefore, to dissolve the precipitate in hydrochloric acid, and reprecipitate it by the addition of ammonia and the magnesia solution.

Analysis of an Insoluble Silicate.*

(*Containing the metals iron, aluminium, calcium, magnesium, potassium, and sodium.*)

Epitome of Process.—The finely powdered silicate is fused with alkaline carbonates (*fusion mixture*). The "melt" is extracted with water, and the silicic acid precipitated with hydrochloric acid, after which the mixture is evaporated to dryness and gently heated. The insoluble silica is filtered off, dried, and weighed. The iron and aluminium are together precipitated as hydroxides, and afterwards separately determined by one of the methods given on p. 278.

The calcium is next separated as calcium oxalate. The filtrate is evaporated to dryness, and heated to expel ammonium salts; the residue is dissolved in water, and the magnesium precipitated as ammonium magnesium phosphate.

The alkalies are estimated in a separate portion by fusion with calcium carbonate and ammonium chloride, whereby they are converted into soluble chlorides. The product is extracted with water; the soluble calcium salts are precipitated as oxalate, and after the removal of ammoniacal salts, the mixed chlorides of potassium and sodium are dried and weighed. The proportion of potassium chloride in this residue is then determined as the double potassium platinum chloride, and the sodium chloride estimated by difference; and from the results so obtained the percentage of potassium and sodium oxides is calculated.

Silica.—From 1·5 to 3 grams † of the silicate (which has been reduced to the finest possible powder,‡ and dried §), are weighed out into a platinum crucible of fairly large dimensions, and intimately mixed with five or six times its weight of fusion mixture by means

* A large number of the common natural silicates (*e.g.* the felspars, micas, hornblende, etc.) consist essentially of varying proportions of silicates of iron and aluminium, calcium, and magnesium, and one or more of the alkali metals. The various kinds of glass are also silicates containing similar constituents, being composed mainly of silicates of sodium (or potassium) and calcium, mixed with varying smaller quantities of aluminium, iron, and manganese. In flint glass the calcium silicate is more or less entirely replaced by lead silicate.

† In the case of such a silicate as felspar, which may contain less than 1 per cent. of some bases, a larger quantity must be employed for the analysis than would be necessary in the case of a substance such as glass.

‡ It is absolutely necessary, in order to ensure the complete decomposition of the silicate, that it should be extremely finely powdered. There should be no grittiness to the touch when it is rubbed between the thumb and fingers, and the whole sample should pass readily through a sieve of fine muslin.

§ The powdered silicate should be freed from any adherent moisture by being heated in the steam-oven before being weighed out for analysis. Some silicates contain *combined* water (e.g. *serpentine*, *meerschaum*, etc.). This should be estimated by heating a weighed quantity of the powdered mineral to redness in a platinum crucible until the weight is constant.

of a stout platinum wire, or a thin glass rod with carefully rounded ends. The entire mixture should not more than half fill the crucible. The covered crucible is then heated over a Bunsen flame, at first gently in order to expel the moisture present in the mixture, and afterwards more strongly until the mass begins to melt round the edges. It is then heated by means of a blowpipe, until the decomposition is complete and the contents of the crucible are in a state of quiet fusion. Care must be taken, by regulating the heat of the blowpipe, to prevent undue frothing of the mass while the carbon dioxide is being evolved; the progress of the operation should be watched by momentarily slightly raising the crucible lid from time to time.

When the operation is complete, the crucible is allowed to cool down, and when cold it is placed upon its side in a beaker with about 100 c.c. of water, care being taken that no impurities are conveyed into the solution upon the outside of the crucible. The beaker is heated upon an iron plate or sand-bath, and the water allowed to boil gently until the "melt" is either entirely detached from the crucible or has become honeycombed by the action of the hot water. Hydrochloric acid is then cautiously added in small portions at a time (the clock-glass cover being partially withdrawn for each addition) until effervescence ceases, and no further precipitation of gelatinous silicic acid takes place. The crucible and lid are then withdrawn * and rinsed into the beaker.†

The mixture is transferred to a dish, and evaporated to dryness upon a steam-bath, the gelatinous mass, as it stiffens, being stirred at frequent intervals with a short glass rod, in order to break it up as much as possible and thus expedite the drying. When the mass has become white and pulverulent, the dish is transferred to an air-bath, and heated to about 160° for half an hour.

The residue is then moistened with a little strong hydrochloric acid, and digested upon the steam-bath for a short time, acid being added as evaporation goes on.‡ Hot water is added, and the silica

* Ordinary brass or iron crucible tongs must not be dipped into this acid liquid. In the absence of platinum or bone-tipped tongs, the crucible can be lifted a little way out of the liquid by means of a glass rod, and the projecting part first rinsed with a drop of water from the wash-bottle, after which the crucible can be taken hold of with the tongs.

† If the fusion has been satisfactorily conducted, there should be no trace of gritty particles at the bottom of the beaker. Should such be detected, it will probably be due to imperfect powdering of the mineral, and in that case the experiment must be set aside, and the operation repeated.

‡ Oxides of iron and aluminium, after being heated, are less easily dissolved by hydrochloric acid, hence the necessity for this step.

washed several times by decantation with hot water, after which it is transferred to the filter and washed until the wash-water is free from chlorides.

The silica is dried in the steam-oven, transferred to a platinum crucible,* and the paper incinerated upon a platinum spiral. The covered crucible is heated, at first very cautiously with a small flame, and afterwards to a red heat, and weighed until constant.†

Iron and **aluminium** are precipitated together in the form of hydroxides by the addition of ammonium chloride and ammonia to the filtrate from the silica. The precipitation is conducted as described on p. 277, and the iron and aluminium are separately estimated by either of the methods given on p. 278. From the results obtained, the percentages of ferric oxide, Fe_2O_3, and aluminium sesquioxide, Al_2O_3, present in the mineral are calculated.

Calcium.—If the filtrate and washings from the precipitated hydroxides of iron and aluminium are more in volume than about 150 c.c., they should be evaporated down to that bulk, and the calcium then precipitated as oxalate, as on p. 231. From the result obtained, the percentage of calcium oxide, CaO, is calculated.

Magnesium.—In the filtrate from the calcium oxalate the magnesium is precipitated in the form of ammonium magnesium phosphate, as described on p. 233.

From the weight of magnesium pyrophosphate obtained, the percentage of magnesium oxide, MgO, is calculated. Factor—

$$(Mg_2P_2O_7)\ 222 : (2MgO)\ 80 = 1 : 0{\cdot}3603$$

Potassium and Sodium.—When the silicate has been "opened up" by fusion with alkaline carbonates as above described, it is obvious that the estimation of the alkalies cannot be made in the solution so obtained; these constituents must therefore be

* The silica obtained in this way is an extremely light powder, which is easily blown away; hence some care is necessary in the manipulation of it, in order to avoid loss from this cause.

† It is always desirable to test the purity of the silica after it has been weighed. In the case of silicates which are liable to contain small quantities of tin, tungsten, niobium, or tantalum, the oxides of these metals will be admixed with the silica, and in such cases an examination of the silica is necessary. For this purpose the contents of the platinum crucible are digested upon a steam-bath with pure aqueous hydrofluoric acid and a few drops of strong sulphuric acid, the operation being performed in a draught cupboard. The silica is thus converted into silicon fluoride, which is expelled. Fresh hydrofluoric acid is added once or twice as the liquid evaporates, after which the contents of the crucible are evaporated to dryness, strongly heated, and weighed. The residue is again submitted to the same treatment until the weight is constant. The loss of weight represents the silica which was present.

determined in a separate portion of the mineral, which is decomposed by another method. About 1·5 to 2 grams of the powdered silicate are weighed into a platinum crucible, and there intimately mixed with about six times its weight of pure precipitated calcium carbonate,* and about its own weight of pure ammonium chloride. The crucible is then gradually raised to a bright red heat, and maintained at that temperature for an hour. This may be accomplished by means of a powerful Bunsen, a plumbago crucible with the bottom out being inverted over the platinum crucible, as shown in Fig. 60.† The crucible is afterwards allowed to cool, and then placed in a covered porcelain dish and digested with water upon a sand-bath. The crucible is withdrawn and rinsed, and the liquid filtered, the residue being thoroughly washed. The solution, which now contains the alkali metals in the form of chlorides, is freed from any lime salts which have dissolved, by the addition of ammonia, ammonium carbonate, and a small quantity of ammonium oxalate. The precipitate is filtered off and washed, and the filtrate evaporated to dryness in a platinum dish upon a steam-bath. The residue in the dish is heated over a small rose burner without raising the temperature to redness, in order to expel all the ammonium salts. It is then dissolved in a small quantity of water, and the last traces of lime which may have escaped precipitation are thrown down by the addition of one or two drops of ammonia and ammonium oxalate. The solution is passed through a small filter, which must be afterwards thoroughly washed, the filtrate and washings being received in a weighed platinum dish. A few drops of hydrochloric acid are added, and the liquid is then evaporated to dryness, heated to expel ammonia, and weighed. It is again heated and weighed, until the weight of the mixed chlorides of the alkali metals is constant.

Fig. 60.

* Prepared by the addition of ammonium carbonate to a solution of barium chloride, and thoroughly washing and drying the precipitate.

† The blowpipe is not so suitable for the purpose, partly on account of the tediousness of using a blowpipe for so long, but more particularly because of the liability to overheat portions of the mixture, and the subsequent risk of loss of alkaline chlorides by volatilisation.

In order to estimate the relative proportions of the potassium and sodium chlorides, the residue is dissolved in a very small quantity of water, and the potassium precipitated and weighed as the double potassium platinic chloride, as described on p. 249. From the weight of the double salt obtained, the weight of potassium chloride is calculated. Factor—

$$(2KCl,PtCl_4)\ 486 : (2KCl)\ 149 = 1 : 0{\cdot}3065$$

And on deducting the weight of potassium chloride so obtained, from the weight of the mixed chlorides, the proportion of sodium chloride is found.

Having found the weights of the two separate chlorides, the percentages of potassium and sodium oxides (K_2O and Na_2O) which they represent is calculated by means of the factors—

$$(2KCl)\ 149 : (K_2O)\ 94 = 1 : 0{\cdot}6308$$
$$(2NaCl)\ 117 : (Na_2O)\ 62 = 1 : 0{\cdot}530$$

NOTE 1. *Alternative Methods for the Estimation of the Alkalies.*—(1) In the foregoing method, it will be obvious that, as the potassium alone is determined, the sodium being estimated by difference, the experimental errors fall more heavily upon the latter alkali. This may be obviated by determining the chlorine (instead of the potassium) in the mixed chlorides. The mixed chlorides are dried and weighed as in the process described above; the residue is then dissolved in water, and the chlorine precipitated as silver chloride by means of silver nitrate. The estimation may be carried out gravimetrically, as described on p. 238, or by the volumetric method given on p. 360.

From the result, by whichever method obtained, *the percentage of chlorine contained in the mixed chlorides* is calculated.

From these data, namely, (W) the weight of the mixed chlorides, and (B) the percentage of chlorine in the mixture, the actual amount of each chloride present can be calculated; thus—

The theoretical percentage of chlorine in sodium chloride = 60·68
" " " " potassium chloride = 47·65

The percentage of chlorine, therefore, in any mixture of these chlorides will obviously lie between these two extremes; the nearer it approaches to one of them, the less of the other chloride will be present in the mixture. Thus, for example, the percentage of sodium chloride in the mixture will rise from 0 to 100 as the percentage of chlorine increases from 47·65 to 60·68, *i.e.* passes through a range of 13·03 per cents. (60·68 − 47·65 = 13·03).

Hence, if the percentage of chlorine in potassium chloride be deducted from the percentage of chlorine found in the mixed chlorides, the result when multiplied by 100 and divided by 13·03 gives the percentage of sodium chloride in the mixture—

13·03 : B − 47·65 :: 100 : x = percentage of sodium chloride in the mixed chlorides

From this the actual weight of sodium chloride found is calculated by the proportion—

100 : W :: x : y = grams of sodium chloride in the mixed chlorides

And then—

W − y = z = grams of potassium chloride in the mixed chlorides

A concrete example will render this perfectly clear—

The weight of the mixed chlorides (W) was 0·64 gram
The percentage of chlorine in the mixture (B) was 50·256

Deducting from B the theoretical percentage of chlorine in potassium chloride, we get—

Percentage of chlorine found	50·256
,, ,, in KCl	47·650
Difference	2·606

Then 13·03 : 2·606 :: 100 : 20·0 = % of NaCl in mixed chlorides
and 100 : 0·64 :: 20 : 0·1280 = grams of NaCl in mixed chlorides

And deducting this from the weight of the mixed chlorides, the weight of the potassium chloride is found ; thus—

	Grams.
Weight of mixed chlorides	0·640
,, sodium chloride	0·128
,, potassium ,, ...	0·512

By multiplying the weights of sodium chloride and of potassium chloride by their respective factors (given above), the weights of the oxides equivalent to the chlorides will be obtained, and from these the actual percentages of Na_2O and K_2O in the silicate are calculated ; thus—

0·128 × 0·530 = 0·06784 = grams Na_2O
0·512 × 0·6308 = 0·32297 = grams K_2O
Weight of silicate taken for analysis = 2·0150 grams
therefore 2·0150 : 0·06784 :: 100 : 3·31 = % of Na_2O in the silicate
and 2·0150 : 0·32297 :: 100 : 15·03 = % K_2O ,, ,,

(2) Another method for the estimation of the alkali metals is an electrolytic process,* by means of which *both* alkali metals can be separately determined. The mixed chlorides are dried and weighed as before,† and the potassium precipitated as the double potassium platinic chloride. The precipitate is washed perfectly free from

* See Section V. p. 292.

† It is not *essential* to weigh the dry chlorides, although a knowledge of their weight serves as a useful check upon the results obtained by the electrolysis.

platinum chloride by means of alcohol ; it is then dissolved in water and the solution submitted to electrolysis, using the current from one Daniell cell. The deposited platinum is washed and dried, and from its weight the weight of potassium chloride present is calculated by means of the factor—

$$(Pt)\ 195 : (2KCl)\ 149 = 1 : 0{\cdot}7641$$

The filtrate from the precipitated potassium platinic chloride contains the sodium chloride mixed with the excess of platinum chloride. It is electrolysed until the whole of the platinum is deposited, and the liquid, now containing only sodium chloride, is transferred to a dish and evaporated to dryness ; after which it is gently heated, and weighed. The weight of sodium chloride thus determined, when added to the weight of potassium chloride calculated from the former operation, should equal the weight of the mixed chlorides.

From the chlorides, the proportion of *potash* and *soda* present in the silicate is calculated as in the previous example.

NOTE 2. *Alternative Method for decomposing the Silicate, by means of Hydrofluoric Acid.*—The finely powdered silicate is treated with strong aqueous hydrofluoric acid (pure) in a capacious platinum crucible, and the mixture digested upon a steam-bath (in a draught chamber) for some time, fresh acid being added once or twice as the liquid evaporates. A few drops of strong sulphuric acid, previously mixed with its own volume of water, are added in order to convert the metals into sulphates, and the mixture evaporated nearly to dryness upon the steam-bath. The crucible is then cautiously heated over a small rose burner (see Fig. 52, p. 248) in order to expel the excess of sulphuric acid. The residue is moistened with a few drops of strong hydrochloric acid and dissolved in water. If the decomposition of the silicate by the hydrofluoric acid has been complete, any undissolved residue will consist of insoluble sulphates (*i.e.* sulphates of lead or the alkaline earths).

SECTION V.

Electrolytic Methods.

The quantitative estimation of metals by the process of electrolysis is based upon the fact that when solutions of certain metallic salts are submitted to the action of an electric current of suitable strength, the metals are precipitated upon the negative electrode in the form of coherent films or deposits. The operation is, in fact, an electroplating process, where the article to be "plated" is a weighed piece of platinum, and the metal with which it is coated is the metal that is to be estimated.

Just as in the familiar process of electroplating with silver, it has been found that a solution of the double cyanide of potassium and silver is the most suitable compound for the purpose, so with the other metals it is only certain of their salts which are adapted for the quantitative deposition of the metal they contain. For example, when a solution of zinc sulphate is electrolysed, the first action of the current (as in other cases) is to separate the salt into its ions. The positive ions, or *cathions* (*i.e.* the zinc atoms), travel to the cathode, or negative electrode, while the negative ions, or *anions* (namely, the (SO_4) groups), go to the anode, or positive electrode; thus—

$$\underset{}{ZnSO_4} = \underset{\text{Cathode.}}{Zn} + \underset{\text{Anode.}}{SO_4}$$

The negative ions, however, at once undergo a secondary decomposition, for in the presence of the water they are converted into sulphuric acid and free oxygen—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2$$

The sulphuric acid thus generated by this secondary action attacks the deposited zinc, and a condition of equilibrium is established when the metal is dissolved as fast as it is deposited; hence complete precipitation of zinc under these conditions is impossible. If, instead of the sulphate, the oxalate (or the double oxalate of zinc and ammonium, as being the more soluble compound) be employed, no such complication from the action of the products of secondary decompositions will arise. The zinc oxalate

is decomposed into zinc and carbon dioxide, while the ammonium oxalate is separated primarily into ammonium (NH_4) and carbon dioxide, and secondarily into hydrogen and hydrogen ammonium carbonate; thus—

Cathode. Anode.

$$ZnC_2O_4 = Zn + 2CO_2$$

$$(1)\ (NH_4)_2C_2O_4 = 2NH_4(= H_2 + 2NH_3) + 2CO_2$$

$$(2)\ 2NH_3 + 2H_2O + 2CO_2 = 2H(NH_4)CO_3$$

The *apparatus* required consists essentially of two platinum electrodes. That which is to serve as the cathode, and receive the deposited metal, is usually made in the form either of a cylinder or, better, a cone; which in either case is riveted or welded to a stout platinum wire, *a*, Fig. 61. The advantage of the conical shape is that loss from spitting, as the gas-bubbles rise to the surface of the liquid, is reduced to a minimum. The anode is conveniently a thick platinum wire bent in the form shown at *b*, Fig. 61.

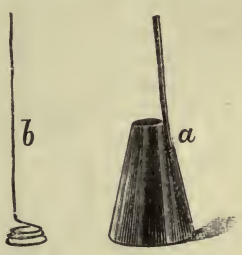

Fig. 61.

When only an occasional analysis is to be made, these electrodes may be supported in a beaker by means of ordinary clamps upon two retort-stands; the beaker being placed upon a wooden block, so that by the withdrawal of the latter the beaker can be lowered and removed. By means of

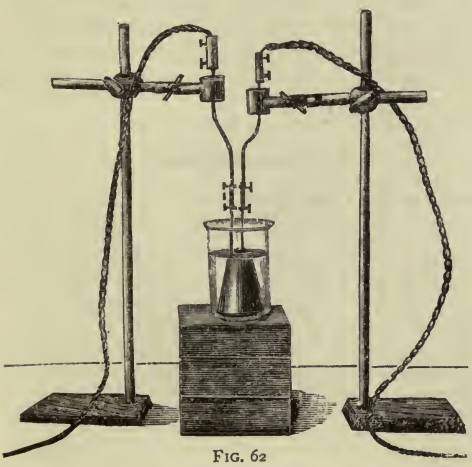
Fig. 62

binding-screws, the electrodes are connected to the wires leading from the battery. The arrangement is shown in Fig. 62.

Instead of conducting the electrolysis in a beaker, it may be carried out in a platinum dish. In this case the dish is made the cathode, by being supported either upon the ring of a retort-stand, or upon any other convenient metal support which is connected to

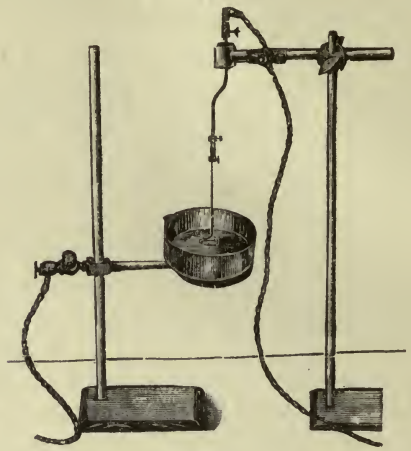

Fig. 63.

the negative wire from the battery ; and the anode, held in a clamp, is lowered nearly to the bottom of the dish, as shown in Fig. 63. The metal to be determined is then deposited upon the dish itself. The deposited metal is ultimately removed from the electrode by solution in a suitable acid.

Typical Examples.*

Estimation of Copper.—About 1·5 gram of recrystallised copper sulphate is weighed out into a beaker and dissolved in 200 c.c. of water. About 2 c.c. strong nitric acid are added,† and the mixture gently stirred with the platinum wire which is to be used as the anode ; this is then left standing in the beaker. The platinum

* Students who wish for a more extended practice in electrolytic methods, should consult Classen's "Quantitative Analysis by Electrolysis," English translation (Herrick). 1894.

† When copper is to be separated from other metals, a larger quantity of nitric acid must be added (see p. 298).

cone, which has been perfectly cleaned * and carefully weighed, is then lowered into the beaker over the projecting end of the anode. The two electrodes are then supported by the clamps, so that they do not touch each other, and are slightly raised from the bottom of the beaker, the anode reaching slightly below the cone, in the manner shown in Fig. 62.

The electrodes are then connected to the battery (the platinum cone being attached to the negative wire), and a current of 0·5 to 1 ampère passed through the solution.† The copper is gradually deposited upon the platinum cone, and the blue colour of the solution becomes fainter and fainter, until at last the liquid appears colourless. The operation takes several hours for its completion, and may be conveniently allowed to go on all night. To ascertain whether the precipitation is finished, one or two drops of the solution are withdrawn by means of a pipette, and a little sulphuretted hydrogen added, which should produce no coloration. The wooden block is then withdrawn, and the beaker lowered away before interrupting the current, the anode at the same time being disconnected and removed with the beaker. The cone is then dismounted, and rinsed with water by means of a wash-bottle. It is then dipped once or twice into a beaker of alcohol, and placed in the steam-oven for a few minutes to dry, and then weighed.

The gain in weight gives the copper in the amount of copper sulphate employed, from which the percentage of copper is calculated. (The result is usually from 0·1 to 0·2 per cent. too low.)

The electrolytic method is one that is much employed in the commercial analysis or valuation of copper ores and of metallic copper, as well as in the estimation of copper in alloys. The analyses are carried out in the following manner :—

I. *In copper ores.*

* It is of the greatest importance that the cathodes used in electrolytic analysis should be absolutely clean and free from the slightest trace of grease, even such as would be contracted by touching them with the fingers.

† When the electric current from a "dynamo" or from storage batteries is employed, it must be reduced to the requisite strength by the introduction of a system of resistance coils. If too strong a current be used, the deposited copper is rough and less coherent. When only an occasional analysis is to be made, two or three Daniell cells may be used. In this case the zinc plate of the battery is the negative, and is connected to the platinum cone. Care must be taken that all the connections are clean, so as to ensure perfect metallic contact. If the electrolysis be conducted in a platinum basin, the latter should be covered, in order to prevent any of the liquid being carried off in the form of fine spray with the gas which escapes from the anode. For this purpose, either a clock-glass, with a small hole bored in the middle to allow the wire to project through, or an inverted funnel of such a size that the mouth will just go inside the dish, may be employed. When the platinum cone is used, the vessel need not be covered.

From 1 to 1½ gram * of the finely powdered ore is weighed out into a porcelain dish, and treated with from 10 to 20 c.c. of strong nitric acid. About an equal volume of dilute sulphuric acid † is then added, and the mixture gently evaporated to about half its bulk in the covered dish. Water is then added, and the insoluble residue (the gangue) is filtered and washed.‡ The filtrate is diluted up to 200 c.c. with water, 10 c.c. of nitric acid added, and the solution electrolysed as described above, with a current from two Daniell cells.§

II. *In commercial copper.*

About 0·5 gram of the metal is weighed out into a beaker, and dissolved in 10 c.c. strong nitric acid, to which an equal volume of water has been previously added. The mixture is boiled in the covered beaker until "nitrous fumes" cease to come off, after which it is diluted up to 200 c.c. with water, and the solution electrolysed. The electrolysis must not be continued longer than is necessary for the complete precipitation of the copper, otherwise traces of antimony and arsenic, which may be present, will also be deposited, which will be evident by the cathode becoming darkened in colour. (For the separation of traces of antimony and arsenic thus deposited, see footnote.) Should the sample of copper contain any silver, this will be deposited and weighed along with the precipitated copper. In this case the silver must be separately estimated (by dissolving 10 to 20 grams of the metal in nitric acid, and precipitating with hydrochloric acid in the usual way, p. 238) and the proportion present deducted from the weight obtained.

Estimation of Zinc.—About 2 grams of crystallised zinc sulphate are weighed out into a beaker, and dissolved in about

* For ores containing less than 25 per cent. of copper, from 1½ to 5 grams may be taken.

† If the ore is a sulphide, the addition of sulphuric acid is unnecessary, since the sulphur is oxidised into sulphuric acid.

‡ Copper ores frequently contain organic matter, in which case this residue will be dark coloured, and is liable to retain a small portion of the copper. If the quantity of this bituminous matter is appreciable, it should be destroyed before treatment with nitric acid, by roasting the weighed quantity of powdered ore taken for the analysis in a porcelain crucible, with free access of air.

§ If more than small quantities of antimony or arsenic are present in the ore, these elements begin to deposit upon the copper towards the end of the operation. When the amount is quite small, they may be separated by strongly heating the electrode. The arsenic volatilises, while the antimony and copper are oxidised; the former oxide volatilises, leaving copper oxide. This is then dissolved in nitric acid and redeposited by the current. When the amount of antimony or arsenic is considerable, this plan cannot be adopted, and, moreover, the precipitation of copper in the presence of much arsenic is incomplete. In this case, a weighed quantity of the finely powdered ore is gently heated in a covered porcelain crucible with about four times its weight of ammonium chloride. Antimony and arsenic are thus converted into chlorides and expelled. The residue is dissolved in nitric acid and treated as already described (Classen. "Zts Anal. Ch.," 18, 388).

50 c.c. of water. Six or 7 grams of ammonium oxalate, dissolved in a small quantity of warm water, are gradually added, with constant stirring.

The solution is then diluted to 150 c.c. and electrolysed. The process is complete when a drop of the solution gives no precipitate when warmed with potassium ferrocyanide upon a watch-glass. The platinum electrode containing the deposited zinc is then removed, thoroughly rinsed with water, and finally with absolute alcohol. It is then placed for a few minutes in a steam-oven to dry, and weighed.

Estimation of Nickel.—About 2 grams of ammonium nickel sulphate, $(NH_4)_2SO_4,NiSO_4,6H_2O$, are weighed out into a beaker and dissolved in water, and the solution rendered strongly alkaline by the addition of ammonia. The volume of the liquid is made up to 150 c.c. with water, and the solution submitted to electrolysis. The process may be allowed to continue all night: it is complete when a drop of the liquid gives no precipitate with ammonium sulphide. The cathode is then washed and dried, and finally weighed, as in the former examples.*

Analysis of Silver Coin.—About 0·5 gram of the metal is weighed out and dissolved in nitric acid (strong acid diluted with an equal volume of water) in a covered evaporating-dish. The liquid is evaporated nearly to dryness upon a steam-bath to expel the acid, and the residue dissolved in water. The solution is then transferred to a beaker, and a moderately strong solution of ammonium oxalate is added. Oxalates of silver and copper are formed; the latter, however, dissolves in excess of the reagent, leaving the insoluble silver oxalate as a white precipitate. The liquid is filtered, and the precipitate washed perfectly free from copper, first with a dilute solution of ammonium oxalate, and finally with water. The copper, contained in the filtrate and washings in the form of the double ammonium copper oxalate, is then precipitated by electrolysis. The precipitated silver oxalate is dissolved in a solution of potassium cyanide, diluted with water to about 150 to 200 c.c., and the solution electrolysed. The electrode with the deposited silver is washed with water and with alcohol, and dried in the steam-oven.

Analysis of German Silver.—About 1 gram of the alloy is

* Nickel may also be precipitated from the solution of the double ammonium oxalate, as described for zinc. In this case, the solution should be maintained at a temperature about 40° to 50° throughout the operation, by means of a small flame placed beneath the beaker. Cobalt and iron may be estimated in the same way.

weighed out into a beaker, and dissolved in about 15 c.c. of strong nitric acid mixed with the same volume of water. The solution is then diluted up to 150 c.c. with water, and submitted to electrolysis. Under these circumstances the copper alone is deposited.* When the precipitation is complete,† the beaker containing the solution is lowered away from the electrodes before the current is interrupted. The cathode with its deposit of copper is rinsed with water (the washing being added to the solution in the beaker), and finally dipped into alcohol and dried and weighed.

The positive electrode is also rinsed into the beaker,‡ and the solution evaporated to dryness in a dish upon a water-bath, with the addition of a little hydrochloric acid, in order to convert the remaining metals into chlorides.

The residue is dissolved in water and a few drops of hydrochloric acid, and the solution transferred to a beaker. Sodium carbonate solution is added until a slight precipitate persists, after which hydrochloric acid is added drop by drop until the precipitate just redissolves. The zinc is then precipitated from this solution as zinc sulphide, as described on p. 244. The washed precipitate is dissolved in the smallest possible quantity of strong hydrochloric acid, and the solution evaporated to expel the excess of acid. The residue is dissolved in water, ammonium oxalate is added (as described on p. 297), and the solution diluted with water to 100 c.c. and electrolysed.§

* It must be remembered that nitric acid is decomposed by the passage of an electric current, nitrogen peroxide and oxygen being evolved at the anode, while hydrogen is liberated at the negative electrode. This nascent hydrogen reacts upon the nitric acid, with the formation of ammonia; thus—

$$HNO_3 + 4H_2 = 3H_2O + NH_3$$

Hence, if the current is allowed to continue passing through the solution after the copper is all precipitated, the nitric acid is gradually decomposed in this manner, and then the zinc in the solution begins to deposit along with the copper.

† A drop of the solution, when tested by adding sodium bicarbonate and potassium ferrocyanide, should give no brown coloration of copper ferrocyanide.

‡ In the analysis of alloys in which traces of lead are present as an impurity, the lead will be deposited as the peroxide upon the positive wire, which will appear brownish or black in consequence. By weighing the electrode with the deposited peroxide, after drying in an air-oven at 110°, the amount of lead present can be calculated.

§ Any traces of iron present in the alloy will be deposited along with the zinc. If the amount is greater than mere traces, it may either be removed before the zinc is precipitated as sulphide (as described on p. 271), or a separate estimation may be made in a larger quantity of the alloy; and the calculated proportion which will have been deposited with the zinc is deducted from the weight obtained of the electrolytic deposit of that metal.

The filtrate and washings from the zinc sulphide contain the nickel, which may be precipitated either from the double ammonium sulphate or oxalate.

(α) *From the Double Sulphate.*—Three or 4 grams of ammonium sulphate dissolved in 10 c.c. of water are added to the solution, and then about 20 c.c. of strong ammonia. The mixture is diluted with water to 100 c.c., and electrolysed as on p. 297.

(β) *From the Double Oxalate.*—Four or 5 grams of ammonium oxalate, dissolved in about 20 c.c. of warm water, are added to the solution, which is then diluted with water to 100 c.c. and submitted to electrolysis, the liquid being maintained at a temperature about 40° to 50° throughout the operation.

Alloys consisting of copper and nickel only, may be analysed electrolytically in the following way: From 0·5 to 0·75 gram of the alloy is dissolved in the minimum quantity of nitric acid (diluted as above), and the solution evaporated to dryness with the addition of a few drops of sulphuric acid. The residue is taken up with water, and again evaporated to dryness with a few drops of sulphuric acid to completely expel the nitric acid. The residue is dissolved in water with a few drops of sulphuric acid, and made up to about 100 c.c., and the solution electrolysed (a current of 0·5 ampère requiring 4 to 6 hours). The electrode is washed and dried and weighed as already described. To the solution 15 c.c. of strong ammonia are added, and the liquid electrolysed with a current of about 0·3 ampère (or three Daniell cells). The nickel will be entirely deposited in about 6 hours.

PART II.

VOLUMETRIC METHODS.

SECTION I.

Preliminary Manipulations.

Introductory Remarks.—In volumetric methods of analysis,* determinations are made, not by weighing a *product* obtained by the interaction of a reagent with the substance to be estimated, but by finding the weight of the *reagent* which it is necessary to employ in order to exactly complete a given chemical interaction with the substance to be determined. For example, in making a *gravimetric* determination of chlorine in a soluble chloride, the chlorine is precipitated as silver chloride by the addition of silver nitrate solution in quantity a little in excess of that which is required to complete the reaction, and the precipitated product of the interaction is washed and weighed. The *volumetric* method, on the other hand, consists in finding the weight of the silver nitrate which is required in order to just exactly throw down the whole of the chlorine as silver chloride. Or again, instead of estimating iron by precipitating the hydroxide, and weighing the sesquioxide obtained by heating this hydroxide, the volumetric method consists in finding the weight of some oxidising agent, such as potassium permanganate or potassium dichromate, which is just exactly required to oxidise the iron from the *ferrous* to the *ferric* state.

The weight of the reagent which is used in a volumetric determination is ascertained by employing a solution of known and definite strength, and measuring the volume of it which is required to carry the chemical change to its completion. Thus, in the above illustration, if the exact strength of the silver nitrate solution be

* The term "volumetric analysis" is here employed in its more restricted sense, as applying to those methods of analysis where the volumes of solutions only are concerned. Strictly speaking, it also includes those analytical processes involving the measurement of volumes of *gases* or *vapours*, but by general custom these are classed together under the head of "gas analysis," and conveniently constitute a separate section of analytical practice.

known, it is only necessary to carefully measure the volume which must be employed for the exact precipitation of the whole of the chlorine, in order to learn the weight of the silver nitrate used, and from this the weight of chlorine precipitated can be calculated.

Similarly, if the strength of the potassium permanganate solution be known, then from the number of cubic centimetres employed, the *weight* of the permanganate which is required to oxidise the iron present can at once be ascertained, and from this the actual quantity of the iron is readily calculated.

In practice these calculations are made once for all when the reagents of known definite strengths, called *standard solutions*, are prepared ; so that the *volume* of such a reagent which is required for the analysis, gives at once the *weight* of the substance being estimated. Thus, in the above examples, the strength of the standard silver nitrate being known, the weight of chlorine which can be precipitated by 1 c.c. is calculated, and this weight multiplied by the number of cubic centimetres employed for an analysis gives the weight of chlorine in the compound. Suppose, for example, that the standard silver nitrate contains 0·017 gram of the salt in every cubic centimetre, this would be capable of precipitating 0·00355 gram of chlorine ; hence 1 c.c. of the standard silver nitrate represents, or is equivalent to, 0·00355 gram of chlorine.

In the same manner, from the known strength of the potassium permanganate solution, the weight of iron which 1 c.c. of it is capable of oxidising can be calculated ; so that when the reagent is employed for the estimation of iron, the number of cubic centimetres used, multiplied by the weight of iron which each cubic centimetre is equivalent to, will give the weight of iron in the portion of the substance being analysed.

The process of carrying out a volumetric estimation by the use of standard solutions, is called *titration ;* thus, a solution of a chloride is *titrated* with standard silver nitrate ; a ferrous salt in solution is *titrated* with potassium permanganate ; and so on. Standard solutions themselves have to be *titrated, i.e.* their chemical value or power has to be determined in order to ascertain their exact strength. They are, therefore, often spoken of as *titrated solutions.*

Classification of Volumetric Methods.—Almost all volumetric processes are based upon one of three principles, and they may, therefore, be conveniently classified in the following manner:—*

* One important process which is not included in this classification, is the estimation of copper by means of potassium cyanide. A description of this method will be found on p. 374.

I. *Methods based upon the neutralisation of alkalies and acids*, known also as methods of *saturation.* These methods are sometimes subdivided into two classes, which are included under the terms *alkalimetry* and *acidimetry*, the one being the converse of the other.

II. *Methods based upon processes of oxidation or reduction.*

III. *Methods based upon precipitation*, either alone or in conjunction with one of the other methods. For example, silver may be estimated by precipitation alone by means of standard sodium chloride. As the precipitate readily settles, the point of completion of the reaction may be determined by the failure of a drop of the standard reagent to produce any further turbidity. Barium, on the other hand, may be determined by precipitation as carbonate (from a neutral solution) by the use of an excess of a standard solution of sodium carbonate. The precipitate is filtered off, and the excess of sodium carbonate in the filtrate and washing is estimated by titration with a standard acid. The excess so found, deducted from the total alkali used, gives the amount required for the precipitation of the barium. Or the precipitated barium carbonate, after thorough washing, is dissolved in an excess of standard hydrochloric acid, and the excess of acid estimated by means of standard alkali. The amount of acid required to dissolve the barium carbonate is thus found, and by calculation the weight of barium is ascertained.

Direct and Indirect Determinations.—In a large number of volumetric analyses, substances are determined by indirect processes ; they are estimated, as it were, by proxy. The difference between direct and indirect processes will be most readily understood from the following illustrations.

Ammonia may be *directly* determined in an ammoniacal salt by heating a known quantity of the salt along with caustic alkali, and causing the whole of the liberated ammonia to pass into, and be absorbed by, a measured volume of standard sulphuric acid. The exact quantity of this acid, which is saturated or neutralised by the ammonia, is then ascertained by titrating the solution with a standard alkali. From the amount of alkali thus used, the excess of sulphuric acid present is ascertained, and this deducted from the total volume of acid gives the quantity which has been neutralised by the ammonia ; and as the weight of ammonia to which each cubic centimetre of the standard acid is equivalent is known, it also gives directly the weight of ammonia present in the ammoniacal salt taken for the estimation.

Indirectly ammonia can be determined by boiling a known

quantity of the ammonium salt with a measured volume of standard caustic alkali, and allowing the ammonia to escape. When the whole of the ammonia has thus been expelled, the excess of caustic alkali is estimated by titration with standard acid. The amount of alkali thus determined, deducted from the original volume employed, represents the quantity of alkali which has been decomposed and converted into a salt of the acid which was originally in combination with the ammonia, *e.g.* if ammonium chloride be the salt employed, then a certain quantity of the standard caustic soda will be converted into sodium chloride, and this gives indirectly the amount of ammonia.

In the direct process we actually estimate the *ammonia*, while by the indirect method we, in reality, determine the quantity of the *acid radical* with which the ammonia is combined, and from this find the ammonia by calculation.

Again, chromium in a chromate may be determined *indirectly* by boiling the salt with hydrochloric acid, whereby chlorine is liberated in the proportion of 3 equivalents of Cl for every 1 equivalent of chromium trioxide, CrO_3 ; thus—

$$K_2CrO_4 + 8HCl = 2KCl + CrCl_3 + 4H_2O + 3Cl$$

The liberated chlorine is made to pass into potassium iodide solution, whereby an equivalent quantity of iodine is liberated, and the amount of iodine so set free is determined by means of a standard solution of sodium thiosulphate (as explained later).

In this process, *iodine* is actually determined, and from this indirectly the chlorine, and yet more indirectly the chromium is estimated.

In order to carry out volumetric analyses, the three following conditions must be fulfilled, namely : (1) the means of accurately measuring the volumes of liquids ; (2) the means of preparing the necessary standard solutions and of testing their accuracy ; and (3) the means of readily ascertaining the exact point when the various chemical reactions involved are complete.

I. **Instruments for Measuring Liquids**.—Graduated glass vessels are employed for measuring the volumes of liquids, four different forms of apparatus being in common use for different purposes, namely, *flasks*, *cylinders*, *pipettes*, and *burettes*.

(*a*) *Graduated Flasks.*—These are flasks of such a size that they shall contain a specified volume of liquid when filled up to a graduation mark upon the neck. They should be provided with a stopper, the neck should be somewhat long and narrow, and the

graduation mark should lie fairly low down upon the neck, in order that the contents of the flask, when it is filled to the mark, may be conveniently shaken up (Fig. 64). The three sizes most convenient for ordinary work are the litre, half-litre, and quarter-litre, besides which a 100-c.c. flask is useful.

FIG. 64.

If one of these flasks be filled with water up to the graduation mark, it will be obvious that when the liquid is poured out, a certain small proportion of it remains behind adhering to the inside of the flask; in other words, the flask does not *deliver* absolutely the whole of the liquid it contained, hence, when such a flask is employed to *deliver* a volume exactly equal to its indicated capacity, it must contain an excess of the liquid equal to the quantity which remains adhering to the glass. Measuring-flasks, therefore, usually contain two graduation marks, the lower one being the mark to which the vessel must be filled in order to *contain* the volume represented by the denomination of the flask, while the one slightly above it indicates the point to which the flask must be filled in order that it shall *deliver* that volume. This applies more especially to the smaller sizes, as the larger vessels are more exclusively used for making up solutions to a given volume. Measuring-flasks are usually graduated at 15° or 15·5° C. (60° F.). Thus, a litre flask is graduated to contain 1000 c.c. of water measured at a temperature of 15·5°, or about the average temperature of the air.* Since, however, liquids undergo an appreciable alteration in volume by change of temperature, their measurements should always be made as nearly as possible at one uniform temperature, otherwise it is

* This volume of water will obviously weigh slightly less than 1000 grams, since 1 gram is the weight of 1 c.c. at its point of maximum density, namely, 4°. Its actual weight is found by multiplying the number of cubic centimetres by the density of water at 15·5° (given in the table in the Appendix); thus, $1000 \times 0{\cdot}99911 = 999{\cdot}11$ grams. Similarly, for a ¼-litre flask, $250 \times 0{\cdot}99911 = 249{\cdot}77$ grams.

If 1000 grams of water at a temperature of 15·5° be placed into a flask, and the volume it occupies be called 1000 c.c., obviously these cubic centimetres are not the true, or, as they are termed, the *absolute* cubic centimetres; they are, of course, slightly greater—greater in the proportion of 1 : 1·00089 (this being the coefficient of expansion of water at 15·5°). In this case, the so-called litre flask would in reality have a capacity of 1000·89 absolute cubic centimetres; and similarly, the ¼-litre flask, while containing 150 of the larger arbitrary cubic centimetres, would hold $250 \times 1{\cdot}00089 = 250{\cdot}22$ absolute cubic centimetres.

necessary to introduce a correction for temperature. For example, suppose a 250 c.c. flask, which has been graduated at 15·5°, is filled to the mark with water having a temperature of 20°, then from the table in the Appendix, giving the coefficients of expansion of water (the volume at 4° = 1), we get the following proportion :—

1·00169 : 1·00089 : : 250 : 249·8 c.c.
(vol. at 20°) (vol. at 15·5°)

hence the volume of liquid measured at the higher temperature is about $\frac{1}{5}$ of a cubic centimetre short. For all ordinary analytical purposes, however, slight variations of temperature to the extent of one or two degrees on either side of 15·5° may be disregarded.

The accuracy of the graduations of measuring-flasks should be tested, *i.e.* the vessels should be *calibrated* before being used. For this purpose the dry clean flask is first counterpoised upon a balance capable of carrying a heavy load. Weights are then placed upon the scale-pan, along with the *tare*, equal to the number of grams of water at 15·5° which the flask is intended to contain.* Water is then poured into the flask (which should be removed from the balance while being filled) until the level of the lowest point of the meniscus (see p. 310) is coincident with the graduation mark. If the flask so filled exactly balances the weights, the graduation may be taken as correct ; if not, water is either withdrawn or added by means of a fine pipette until equilibrium is established, and a fresh graduation is made upon the neck by means of a scratching diamond or a file.

In order to graduate a flask to *deliver* a definite volume, exactly the same procedure is carried out, except that the flask, instead of being *dry* at the beginning, is first filled with water to the mark, and then emptied out and allowed to drain for a few moments (as

* In graduating or calibrating measuring-flasks, one of two plans may be adopted—

(1) The number of grams of water *equal to the denomination of the flask* at 15·5° (or any other temperature which would be more suitable under special climatic conditions) are carefully weighed out, and the volume which they occupy in the flask is indicated by a mark scratched upon the neck. The cubic centimetres in this case have an arbitrary value, as explained in the footnote on p. 304, but if all the measuring vessels are graduated on the same system, so that this arbitrary unit has the same value in them all, no error will arise on this account.

(2) A quantity of water at 15·5° is weighed out, which, if cooled to 4°, would then occupy a volume equal to the denomination of the flask. The number of grams to be weighed out is ascertained by multiplying the denomination of the flask by the density of water at 15·5°, as explained in a previous footnote. In this case, the cubic centimetres represent the true or absolute cubic centimetres. The first method of graduating is the one most usually adopted.

long as it would be allowed to drain when being actually used to deliver). The flask is then counterpoised with the remaining traces of water adhering to the interior surface of the glass.

(*b*) *Graduated Cylinders.*—These are sometimes used instead of flasks, when less accurate measurement is all that is necessary. Two forms are in common use, as shown in Fig. 65, the larger stoppered vessel being known as a *test-mixer*. As shown in the figure, these cylinders are graduated throughout their length into a number of small subdivisions of the total capacity. The correctness of these graduations may be tested by introducing successive

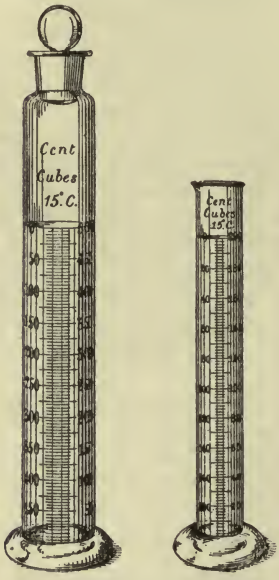

Fig. 65.

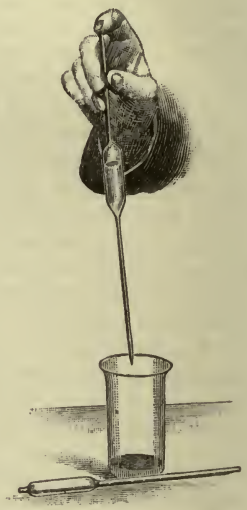

Fig. 66.

small volumes of water from a pipette or a burette, which has been previously tested. If the graduations upon the cylinder do not coincide with the volumes which are thus introduced, a table must be drawn up giving the actual value of each graduation.

(*c*) *Pipettes.*—The pipette is a glass tube, usually with a bulb or enlargement upon it, drawn to a point at one end. Fig. 66 shows the most usual forms of a small and a large pipette. The instrument is graduated to *deliver* its specified volume of liquid.

It is filled by sucking the liquid up until it is somewhat higher than the graduation mark upon the stem, and covering the upper end with the finger, as shown in the figure. Then, by a slight release of the pressure of the finger, the liquid is allowed to flow slowly out, until the level is coincident with the mark upon the stem.

When the pipette is allowed to empty itself, the last drops which remain in the pointed end may either be blown out, or made to flow out by drawing the point along against the wet sides of the vessel into which the liquid is being delivered. The former plan is the quicker, and is the one which is most instinctively resorted to; but the latter is the more accurate method. It is not a matter of serious importance which method is adopted, so long as the *same plan is uniformly employed.*

Pipettes are calibrated to deliver a definite volume by a method practically the same as in the case of flasks. To carry it out, the pipette is first filled with water by suction, and the end of the tube which was dipped into the water is wiped dry on the outside. The liquid is then allowed to run out, and the last drops removed by one of the above-mentioned plans. The point of the instrument is now closed by placing a minute fragment of wax* upon it, and then just softening the wax by bringing the point near to a small flame. In this way the pipette can be closed without the wax entering the tube. The moist pipette is then placed upon a balance and counterpoised.

It is next filled with water at a temperature of 15·5°, which can be introduced by means of a glass tube drawn out sufficiently fine to pass down the stem of the pipette. After the first few drops have been put in, the air-bubble which is usually trapped in the bottom of the tube may generally be dislodged by a few shakes; if this fails, however, it may be removed and the water made to run right into the point by thrusting a long capillary tube down to the bottom. Care must be taken, however, that no fragments of this fine tube become broken off and left in the apparatus. During the filling process the pipette should be supported by a clamp, and not held in the warm hand, otherwise the temperature of the water may be considerably raised during the operation. When the water is coincident with the graduation mark, the instrument is carefully laid upon the scale-pan (the water will not run out of it, although placed in a horizontal position), and gram weights equal to the number of cubic centimetres the pipette is intended to deliver are

* The black bituminous material known as "bicycle cement" answers admirably for this purpose.

placed upon the opposite pan. If this is found to exactly counterpoise the apparatus, the graduation may be taken as correct; but if not, water must be either withdrawn or added, as the case may be, until the apparatus is exactly equipoised, and a fresh mark scratched upon the stem.

(*d*) *Burettes.*—The burette is a long straight glass tube, one end of which is drawn down and terminated by a glass stop-cock, or connected to a jet by means of a caoutchouc tube which can be closed by means of a pinch-cock. Fig. 67 shows the two forms of apparatus. The burette is graduated almost throughout the entire length, the graduations being usually tenths of a cubic centimetre, as shown in Fig. 68. The size most commonly used has a capacity of 50 c.c. For ordinary use the common retort-stand and clamp shown to the left in the figure make a very convenient stand for holding burettes. If desired, several can be supported upon the same retort-stand. The instrument is filled by means of a small funnel placed in the top (which should be removed afterwards, lest any adhering drops fall into the burette), until the liquid is considerably above the topmost graduation. The tap or pinch-cock is then momentarily opened, in order that the liquid may sweep out before it the air which is contained in the tap and jet. This will not be successfully accomplished if the tap or pinch-cock is only *gradually* opened, as the liquid then slips down the walls of the narrowed portions and leaves air-bubbles in the tubes, which it is absolutely necessary to remove before the instrument can be used with exactness.

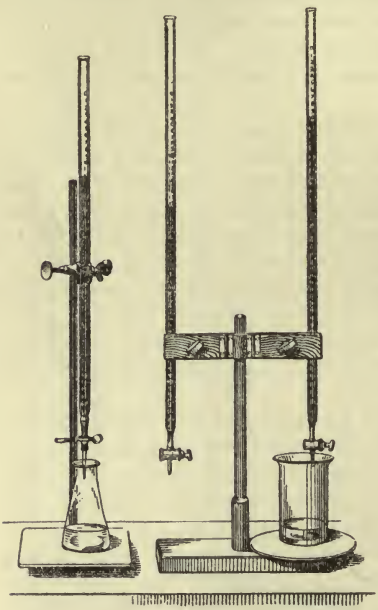

FIG. 67.

The calibration of a burette is a more serious operation than that of a pipette, for since it is obviously out of the question to

regraduate the instrument, the true value of the graduations upon it must be ascertained, and a special table constructed for each instrument. The process is carried out in the following way : The burette is filled with water at a temperature of 15·5° (if possible in a room having that temperature, since the operation occupies a considerable time), the air-bubbles being swept out as described, and the level of the liquid being coincident with the topmost graduation. A clean, dry, stoppered flask, capable of containing as much liquid as the burette, is accurately counterpoised, and the water in the burette is delivered into it in successive small quantities of 3, 4, or 5 of the c.c. graduations at a time. After each small portion of water has been run into it, the flask is weighed until the whole 50 c.c. has been delivered.

The number of grams which each portion weighs, represents the number of cubic centimetres it actually occupies, and if this is different from the number of c.c. graduations, the error is equally divided between them.* Thus, suppose the water is delivered in portions represented by five of the c.c. divisions, and the first portion is found to weigh 5·15 grams, instead of exactly 5 grams ; then the error, namely 0·15, is divided equally among the five graduations, each one of which will then have the value, not of 1 c.c., but 1·03 c.c. The table, therefore, will run as follows for the first five graduations—

Graduation 1 = 1·03 c.c.
„ 2 = 2·06 „
„ 3 = 3·09 „
„ 4 = 4·12 „
„ 5 = 5·15 „

Suppose, after the second portion has been delivered, the weight of the water is 10·17 grams ; then—

10·17 − 5·15 = 5·02 grams = the weight of the second portion of water,

and $\frac{5·02}{5}$ = 1·004 c.c. = the value of each graduation between 5 and 10

hence the table will continue—

* It will be evident that the larger the volume which is delivered at one time, the less accurate is the calibration. Thus, from the above illustration, if instead of delivering the contents of five graduations, that of ten had been weighed at once, the value of each graduation would have been—

$$\frac{10·17}{10} = 1·017$$

and the value of the fifth graduation would have come out—

1·017 × 5 = 5·085 c.c. instead of 5·15

Graduation 6 =	5·15 +	1·004 =	6·154 c.c.
„ 7 =	„ +	1·008 =	7·158 „
„ 8 =	„ +	1·012 =	8·162 „
„ 9 =	„ +	1·016 =	9·166 „
„ 10 =	„ +	1·020 =	10·170 „

Small burettes holding 10 c.c. are sometimes used after the manner of a pipette. They consist of straight tubes drawn to a point at one end, and graduated into tenths of a cubic centimetre, as in the burette. They are filled by suction, and employed as pipettes for delivering various small measured volumes.

Reading the Volume of Liquids in Graduated Vessels.—Owing to the action of capillarity, the surface of a liquid contained in a glass-tube is not *plane*, but *curved*, the extent to which it is curved depending (for the same liquid) upon the diameter of the tube.

This curved surface is called the *meniscus*. Figs. 68 and 70 show the meniscus in the case of water contained in a burette.

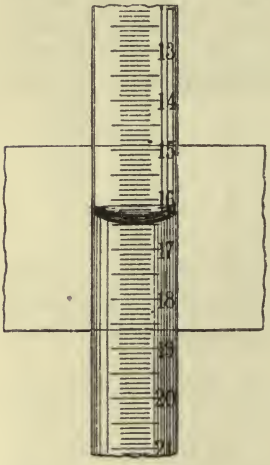

Fig. 68.

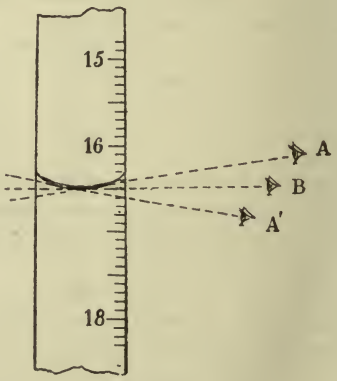

Fig. 69.

In reading graduated instruments, it is usual to take the graduation which coincides with the lowest point of the meniscus. Thus, in Figs. 68 and 70 the volume of the liquid would be taken as 16·5. If, as sometimes happens in certain lights, the line of the curve is not very clearly visible, it may usually be made quite distinct by

holding behind the tube a piece of white paper, inclining it slightly upwards, as in Fig. 68. In order to make a correct reading, it is necessary that the eye of the observer should be in the same horizontal plane as the surface of the liquid. The reason for this will be evident from the diagram (Fig. 69), where an error of one graduation would arise by reading from the positions A or A^1 instead of from B.

Where the graduation mark is continued as a ring right round the vessel, as is usually the case with pipettes and flasks, the eye will be situated in a horizontal plane with the graduation, when the front of the mark exactly overlays the back, so that the *ring* appears as a *line*. The lowest point of the meniscus must then just touch this line. A simple device to ensure that the readings of a burette (where the graduations are on one side of the tube only) shall be consistently made from a correct point of observation is shown in Fig. 70. It consists merely of a narrow strip of card folded in the middle, with the two free ends pinned together with a paper-fastener. This is slipped over the burette, and while it allows of being easily slid up and down the tube, it will also hold itself in any position in which it may be put. When taking a reading, this little clip is placed so that its upper edge is just a little below the level of the liquid : then, when the eye is in such a position that the back and front edges of the clip just coincide, it will also be practically in the same horizontal plane as the bottom of the meniscus.

The same object may be gained by the use of floats. These are little weighted glass bulbs or tubes which are placed inside the burette, floating upon the liquid. The graduation which coincides with the horizontal ring-mark upon the float is the one which is read. Two forms of floats are seen in Fig. 71. A represents the most familiar shape. Unless some care is exercised, the use of such a float is very liable to introduce errors. If it is much narrower than the burette, it may sometimes take up positions in which the graduation mark upon it is not perfectly horizontal. On the other hand, if it is too close a fit, it is very prone to lag behind the liquid, or even to stick altogether. B (Fig. 71) represents a newer and better form of float. Owing to its shape it always maintains a vertical position, and may therefore be sufficiently narrow at its widest point to admit of perfect freedom of movement in the burette. The graduation mark on this float is upon the smaller bulb at the top, which projects above the liquid altogether, hence this form of apparatus may be used equally well whether the liquid

in the burette is colourless or even opaque. The reading, as the float stands in the figure, is 14·4.

It is very necessary, whatever float is used, to keep a close watch upon it as the liquid in the burette gets down towards the bottom graduations. It is well to place an indiarubber ring or other convenient mark upon the burette at the point beyond which it is not admissible to go when the float is being used.

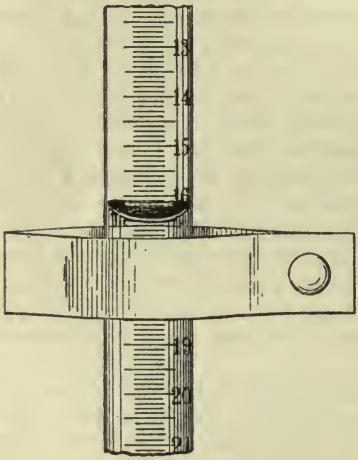

FIG. 70.

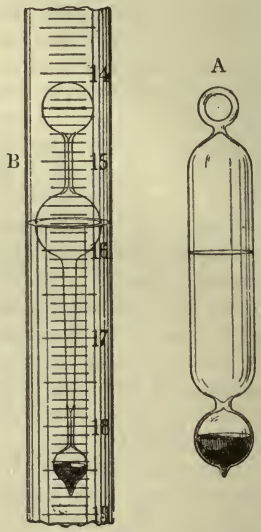

FIG. 71.

II. **Standard Solutions.**—Solutions of known strength which are used in volumetric analysis are called *standard solutions.* These various solutions are usually made of such strengths that the quantities of the positive or negative constituents, or of what may be called the *active* constituents, of the compounds in the solutions shall bear the same relation to each other as the numbers which express their *chemical equivalence*—that is to say, equal volumes of the different solutions will contain *equivalent proportions* of the effective substances in solution.

For example, standard solutions of sodium chloride and silver nitrate will be of such strengths that whatever volume of the former contains 35·5 grams of chlorine, the same volume of the other shall contain 108 grams of silver ; or, again, standard solutions of

hydrochloric acid, of sodium hydroxide, and of sodium carbonate will be of such strengths that whatever volume of the first contains 1 gram of hydrogen, the same volume of the others shall each contain 23 grams of sodium.

Normal Standard Solutions.—When the solutions are of such a strength that the particular volume which contains 1 gram of hydrogen, 23 grams of sodium, 35·5 grams of chlorine, etc., is one litre, then the solution is known as a *normal solution*. Thus, a normal solution of hydrochloric acid will contain 1 gram of hydrogen in the litre, therefore it must contain $\overset{H}{1} + \overset{Cl}{35{\cdot}5} = 36{\cdot}5$ grams of HCl in that volume. Again, normal caustic soda will contain 23 grams of sodium per litre, therefore it must contain $\overset{Na}{23} + \overset{H}{1} + \overset{O}{16} = 40$ grams of NaHO in the 1000 c.c. Or, again, normal sodium carbonate must also contain 23 grams of sodium per litre; therefore the volume must contain $\frac{\overset{Na_2}{46} + \overset{C}{12} + \overset{O_3}{48}}{2} = 53$ grams of Na_2CO_3.

Similarly, if normal sulphuric acid is to be of such a strength that 1 litre shall contain 1 gram of hydrogen, or, in other words, that the amount of the negative radical SO_4 shall be the chemical equivalent of 1 gram of hydrogen, then the litre must contain $\frac{\overset{H_2}{2} + \overset{S}{32} + \overset{O_4}{64}}{2} = 49$ grams of H_2SO_4.

In some cases, it is only a *portion*, and not the *whole*, of some particular element or radical present in the solution, which takes an active part in the chemical reactions for which the solution is used. Thus, in the case of potassium dichromate, $K_2Cr_2O_7$, only three out of the seven oxygen atoms contained in the salt are *available* for purposes of oxidation. We may regard the compound as breaking up into $K_2O,Cr_2O_3,3O$. A *normal* solution, therefore, of this salt (that is, one which shall contain per litre a weight of available oxygen chemically equivalent to 1 gram of hydrogen) must contain $\frac{\overset{K_2}{78} + \overset{Cr_2}{104{\cdot}8} + \overset{O_7}{112}}{6} = 49{\cdot}13$ grams of the salt in every 1000 c.c. The formula-weight of the salt, in this instance, being divided by 6 instead of by 3, because the equivalent of oxygen is 8, and not 16.

Again, the *available* oxygen in potassium permanganate is five out of eight atoms, $2(KMnO_4) = K_2O,2MnO,5O$. Hence a normal solution of this salt, containing in the litre a weight of available oxygen equivalent to 1 gram of hydrogen (*i.e.* 8 grams of available oxygen), must contain in that volume of the solution a weight of salt in grams equal to *one-tenth* of the formula-weight $K_2Mn_2O_8$, or *one-fifth* of that of $KMnO_4$, namely, $\frac{158}{5} = 31{\cdot}6$ grams.*

Solutions of *one-half*, *one-tenth*, and *one-hundredth* of the strength of a normal solution are called respectively *semi-normal*, *deci-normal*, and *centi-normal* solutions, and are distinguished by the signatures $\frac{N}{2}$, $\frac{N}{10}$, and $\frac{N}{100}$.

In preparing standard solutions, the weighed quantity of salt is not added to and dissolved in the measured volume of water, but it is first dissolved in a moderate quantity of water, and the solution afterwards diluted up to the requisite volume by the addition of water. At first sight it might be supposed that the two processes would give the same result, but this is not the case, because the act of solution of many substances is attended by a change (usually a contraction) in the volume, and therefore in one case the solution obtained would be different in volume, and therefore in strength, from that prepared in the other way.

Further details for the preparation of the various standard solutions will be given in the sections devoted to the special analytical processes for which the solutions are employed.

(III.) **Methods for ascertaining the Completion of Volumetric Reactions.**—It is essential to the success of a volumetric process that the exact point when the chemical reaction is complete should be readily determinable. This is usually accomplished by means of a third substance, known as an *indicator*, which is effected in some visible way either by the volumetric reagent or by the solution of the substance being estimated. For example, in order to determine the exact point when an alkali has been neutralised by an acid, a small quantity of litmus solution may be added

* Some chemists, unfortunately, apply the term *normal* to solutions which contain in one litre the formula-weight in grams (*i.e.* the gram-molecule) of the compound. According to this method, while a normal solution of caustic soda contains 23 grams of sodium per litre, the normal sodium carbonate will contain 46 grams of sodium in the same volume. To prevent confusion, these solutions should be distinguished from the true normal solutions by the name *molecular solutions*.

to the solution. Again, the point of complete precipitation of chlorine by means of standard silver nitrate, can be ascertained with exactness by adding a small quantity of a solution of potassium chromate to the solution containing the chloride to be estimated. The silver combines by preference with the chlorine, forming silver chloride ; but when the whole of the chlorine has been precipitated as silver chloride, then the silver attacks the chromate, precipitating the red silver chromate—hence the production of a red precipitate which persists, is the sign that the precipitation of the *chlorine* is complete. The reagent, or standard solution, may itself be the indicator ; this is the case, for example, with potassium permanganate, in which the characteristic violet colour of the solution serves to show the precise moment when the oxidising process is complete. Very often an *outside* indicator is made use of ; that is to say, instead of adding the indicator to the solution which is being tested, the progress of the reaction is watched by removing a drop of the liquid upon a glass rod at frequent intervals, and applying it to the indicator. Thus, in estimating the chlorine in bleaching powder by the oxidation of sodium arsenite, the indicator employed is a mixture of potassium iodide and starch, which gives the characteristic blue colour when in contact with chlorine. The iodide, however, cannot be added to the solution of bleaching powder, but by bringing a drop of the latter into contact with potassium iodide and starch paper until it no longer produces the blue coloration, it is easy to hit the exact point when the oxidation of the arsen*ious* salt into the arsen*ic* state is completed.

Similarly, the point when a ferrous salt is completely oxidised to the ferric condition by means of potassium dichromate, is ascertained by withdrawing a drop of the mixture upon a glass rod and applying it to a drop of potassium ferricyanide solution upon a white plate or porcelain tile ; so long as any ferr*ous* salt is present, a blue coloration is produced, but as soon as the iron is entirely oxidised, a drop of the solution so applied to the ferricyanide indicator will produce no coloration.

SECTION II.

Volumetric Methods based upon Saturation.

Alkalimetry and Acidimetry.

Normal Alkalies and Acids.—The four following standard solutions may be prepared, namely, normal sodium carbonate, sodium hydroxide, sulphuric acid, and hydrochloric acid.

In preparing such a series of solutions, it is necessary to select one of them as the foundation or basis for the others; and the conditions which must be fulfilled by the one which is chosen for this purpose are, that it admits of being made up with the utmost possible accuracy. Of these four solutions the alkaline carbonate is the one which most satisfactorily fulfils these requirements, for it is a salt which can readily be obtained in a state of practical purity, and it also admits of being weighed with perfect exactness.

Having once obtained a normal solution of sodium carbonate of exact strength, it can be employed as a basis for the preparation of normal sulphuric and hydrochloric acids, and by means of either of these the standardisation of the caustic alkali may be effected. The strength of the acids can be checked, if desired, by precipitation (the one with barium chloride, and the other with silver nitrate) and gravimetric determination.

Indicators.—There are a number of substances which may be employed in order to indicate the exact point of neutrality, or the *end reaction*, as it is termed, in processes of alkalimetry and acidimetry. The most important and useful* are *litmus*, *methyl orange*, and *phenolphthalein*.

Litmus Solution.—This is prepared by crushing about 10 grams of the solid in a clean mortar with hot distilled water. The liquid is poured off, and the residue further extracted by one or two fresh supplies of hot water. The extract is then allowed to settle for some hours, and the clear blue liquid, diluted to about 200 c.c., is

* For a full account of the various indicators, their relative sensitiveness, and special uses, see Thomson, *Chem. News*.

transferred to a bottle. As this solution loses its colour if closely corked or stoppered up so as to exclude the air, it is a good plan to place in the neck of the bottle a flat-topped stopper which drops in quite loosely, and serves merely as a cover to prevent the entrance of foreign matter. A few drops of chloroform added and shaken up with the solution, will prevent mould from forming in it, which otherwise the liquid is very prone to develop.

Litmus solution is turned red by acids, and blue by alkalies; the colour which it should exhibit when perfectly neutral is *violet;* it is usually necessary, therefore, to add a drop or two of very dilute acid (preferably nitric acid) by dipping a glass rod into the acid and stirring it into the litmus until a purple or violet tint is imparted to the solution.*

When carbon dioxide is disengaged (as when an alkaline carbonate is being titrated with an acid, or *vice versâ*), litmus cannot be employed as the indicator *unless the liquid be boiled.* This is owing to the fact that the dissolved carbon dioxide itself exerts a feeble acid reaction upon the litmus, and it is only when the gas is entirely expelled by boiling that the litmus becomes the true indicator of the point of neutrality. It is under these circumstances that methyl orange is the more convenient indicator.

Methyl Orange.—This substance dissolves in water, giving an orange-coloured solution, which is turned yellow by alkalies and a pink-red colour by acids. The solution for use as an indicator is prepared by dissolving 0·5 gram of the solid in 500 c.c. of water; and one or two drops only should be employed, as its indications are less sensitive if much of it be used.

Methyl orange is unaffected by carbon dioxide; it is, therefore, specially adapted for titrations of alkaline carbonates with mineral acids, or *vice versâ.* With this indicator, therefore, these determinations can be carried out in the cold.

Methyl orange is only suitable as an indicator where *mineral* acids are concerned; it cannot be used with organic acids.

Phenolphthalein.—A solution of this compound is prepared by dissolving 1 gram of the solid in 100 c.c. of alcohol. The dilute neutral solution is colourless, but on the addition of an alkali it

* The aqueous infusion of litmus obtained in this way contains other things besides the blue colouring matter, and the presence of these tends to diminish the sensitiveness of the reagent. The saline substances may be removed by acidifying the extract with hydrochloric acid, and submitting the mixture to the process of dialysis. The purified colouring matter which remains behind on the dialyser is then dissolved in hot water. It is only for very special purposes, however, that it is necessary to prepare such a purified litmus solution.

becomes a deep red colour. This colour is immediately discharged when the liquid is acidified either with mineral or organic acids.

The chief value of this indicator lies in its applicability to the titration of organic acids. It cannot be employed in cases where carbon dioxide is evolved, since its colour is destroyed by carbonic acid; but as the acid carbonates (bi-carbonates) do not give the red colour with this compound, it can be made use of to indicate the completion of the *first stage* in the neutralisation of a normal carbonate, namely, the conversion of the normal into the acid carbonate. Phenolphthalein cannot be used in the presence of ammonia.

Normal Sodium Carbonate.

(53 *grams of* Na_2CO_3 *per litre.*)

In order to obtain this salt in a state of purity, it is prepared by heating the purest sodium bicarbonate to a dull red heat until no further loss of carbon dioxide and water takes place.* Theoretically, 84 grams of bicarbonate should yield 53 of the normal salt; a slight excess of this proportion, therefore, should be employed. To prepare half a litre of the standard solution, about 43 grams of the pure sodium bicarbonate are heated in a weighed platinum dish to a low red heat for about 10 or 15 minutes. The salt must not be allowed to fuse. It is then cooled in a desiccator and weighed. To ensure that the decomposition has been completed, the dish is again heated for another 10 minutes, and, after cooling in the desiccator, weighed again. The weight of the salt (after deducting the weight of the dish) will be a little over 26·5 grams. By means of a clean spatula or pen-knife, a small quantity is removed, so as to bring the weight to exactly 26·5 grams, the operation being performed without undue exposure of the dry salt. The contents of the dish are then washed out into a beaker, the dish being

* Owing to its much slighter solubility in water, the bicarbonate is the more easily purified salt; hence of the two so-called "pure" salts of commerce, the bicarbonate will have a higher degree of purity than the normal salt. The sample employed here, however, must first be tested in the following way: A few grams are dissolved in a small quantity of hot water, which at once reveals the presence or absence of any traces of insoluble impurity. The solution is then acidified with nitric acid (which must be absolutely free from either hydrochloric or sulphuric acid), and tested for chlorides and sulphates in the usual way. If the salt does not dissolve to a perfectly clear solution, and is not free from chlorides and sulphates, a quantity of it must be purified by recrystallisation. A hot saturated solution is made, and filtered by the use of one of the arrangements for warming the funnel shown on p. 210. The filtered liquid is continually stirred as it cools, whereby the salt is deposited in a fine granular condition. The mother-liquor is then decanted, and the crystals drained and dried upon a porous plate.

thoroughly rinsed with warm water, and the salt completely dissolved by stirring the mixture with a glass rod. The solution is then carefully poured into a half-litre flask, the beaker being several times rinsed with water. The liquid is then cooled to 15·5°, and water at the same temperature is added, with continual gentle shaking, until the neck is reached. The vessel is then carefully filled to the graduation mark, after which the stopper is inserted, and the contents thoroughly mixed by shaking.

Instead of bringing the weight of the sodium carbonate to the exact quantity required for half a litre of solution, the whole of the salt in the dish may be employed, and the exact volume of water which will be required in order to make the solution of normal strength is calculated. Thus, suppose the weight of sodium carbonate in the dish after heating is 26·749 grams, instead of 26·5 ; then—

26·5 : 26·749 : 500 c.c. : 504·7 c.c.

Hence, after the solution has been made up to the graduation mark in the manner described above, 4·7 c.c. of water are added from a burette, and the solution then finally shaken up to ensure thorough mixing.

Normal Sulphuric Acid.

(49 *grams of* H_2SO_4 *per litre.*)

The specific gravity of ordinary oil of vitriol being about 1·8 49 grams will be rather less than 30 c.c. Hence, if this volume be measured out and diluted up to a litre, a solution will be obtained which will have a rough approximation to the required strength. If this solution is then titrated with the standard sodium carbonate, its actual strength can be ascertained ; and by calculation, the volume of water which must be added in order to bring it to the exact normal strength is determined.

Dilution of the Acid.—Thirty cubic centimetres of pure sulphuric acid are gradually poured into about 150 c.c. of water in a flask. The mixture is then cooled by holding the flask under the water-tap, and allowing a stream of water to run over it, at the same time shaking the liquid round within the vessel. When cold, the solution is transferred to a litre flask,* and the volume made up to the 1000 c.c. mark by the addition of water at a temperature of 15·5°.

* It is not advisable to dilute the strong acid in the litre flask itself, as there is always *some* risk (although perhaps not much when experience has been gained) of fracturing the vessel ; and it is obviously wiser that a common flask, and not one which has been carefully graduated, should take this risk.

Titration of the Acid.—A burette is first filled with the dilute acid,* care being taken to remove all air-bubbles from the tap, as explained on p. 308. Twenty-five cubic centimetres of the normal sodium carbonate are then transferred by means of a pipette * to a small beaker, and a single drop of the methyl orange indicator (see p. 317) is added. The beaker is then placed upon a white glazed tile beneath the burette, and the acid gradually run into the alkaline liquid, the solution being gently rotated in order to ensure thorough mixing after each addition of acid. At first 2 or 3 c.c. of the acid may be added at a time; but as the point of neutrality is approached, smaller and smaller quantities are added at once, until they are reduced to a few drops only, and at last the addition of a single drop produces a permanent red colour in the liquid.

Correction of the Acid.—The exact volume of the acid which has been used in order to neutralise the 25 c.c. of normal sodium carbonate is noted, and from it the volume of water which must be added in order to make the acid exactly normal is calculated. Thus, suppose instead of 25 c.c. of acid, 23·8 c.c. were used in neutralising 25 c.c. of the normal alkali; then—

$$25 : 23{\cdot}8 :: 1000 : 952$$

That is to say, 952 c.c. of the acid contain as much sulphuric acid as should be contained in 1000 c.c., if it were exactly normal. If, therefore, 952 c.c. of this acid be measured out into a litre-flask, and the volume be then made up to the litre by the addition of water, a correct normal acid will be obtained.

The solution thus obtained should be once more titrated with the sodium carbonate.

When the strength of the acid is very nearly, but not exactly, normal, instead of attempting to bring it to the precise normal strength, it may be used as it is, and a correction introduced every time by means of a factor. For example, suppose 25 c.c. of normal sodium carbonate required 24·4 c.c. of the acid instead of 25 c.c. in order to neutralise it, then—

$$24{\cdot}6 : 25 :: 1 : 1{\cdot}016$$

That is to say, every cubic centimetre of this acid is equal to 1·016 c.c. of an exactly normal acid; therefore, if the number of

* Whenever burettes or pipettes are employed for measuring standard solutions, they must either be *dry* before use, or, if moist, they must be first rinsed out with a small quantity of the solution; otherwise that portion which is measured out for use would be slightly diluted by the water adhering to the walls of the instrument.

cubic centimetres of this acid used in any titration be multiplied by the factor 1·016, the result will be the number of cubic centimetres which would have been required if the acid had been strictly normal.

Or again, if the acid should be a little *weaker* than the exact normal, a similar correction can be made. Thus, suppose 25 c.c. of normal sodium carbonate required 25·2 c.c. of acid instead of 25 c.c. in order to reach the neutral point, then—

$$25{\cdot}2 : 25 :: 1 : 0{\cdot}992$$

That is to say, each cubic centimetre of the acid is in reality only equivalent to 0·992 c.c. of normal acid, therefore in this case 0·992 is the factor by which the number of cubic centimetres of this acid which might be used, would have to be multiplied in order to convert them into cubic centimetres of normal acid.

Titration of the Acid, using Litmus as Indicator.—In the absence of methyl orange, the titration of the acid by means of sodium carbonate may be carried out with litmus as the indicator. In this case, however, it is necessary to boil the solution in order to expel the carbon dioxide. The acid is added gradually, until the colour of the litmus changes from blue to purple-red. The solution is then boiled, and as the carbon dioxide is expelled the colour returns to the original blue shade. After boiling for a few minutes, acid is admitted in small quantities, and the liquid boiled up after each addition, until at last the addition of a single drop gives a permanent bright-red colour, which does not change on boiling.

As a check to the result thus obtained, the following method may be carried out. After noting the volume of acid which has been used in order to reach the point of neutrality, a measured volume of acid in excess is run into the beaker from the burette, and the mixture (which for this purpose is more conveniently contained in a flask than in a beaker) quickly cooled. This excess of acid is then titrated back with normal caustic soda, which (since no carbon dioxide is evolved) can be carried out in the cold. From the amount of caustic alkali used, the actual volume of free acid present is ascertained. If the former titration was correct, this should exactly agree with the measured excess volume which was added; and if not, it gives the amount of acid which, in the first operation, had been added beyond what was actually necessary for neutrality.

Control Experiments.—The titration of the normal sul-

phuric acid may be checked by either one or both of the following experiments, which should be made in duplicate—

(1) A small quantity, say 3 or 4 grams, of pure sodium bicarbonate is heated in a weighed platinum crucible until the weight is constant, as described above in the preparation of normal sodium carbonate solution. The contents of the crucible are then dissolved in water, and washed into a beaker. This solution is then titrated in the cold with the standard acid, using methyl orange as indicator; or, if litmus is employed, the titration is conducted in the boiling solution. From the result, the exact strength of the acid is calculated as follows: Suppose the weight of sodium carbonate obtained after heating the bicarbonate was 2·66 grams, and that this weight required 50 c.c. of the acid for complete neutralisation, then—

$$53 : 2{\cdot}66 :: 49 : 2{\cdot}459 \text{ grams} = \text{weight of } H_2SO_4 \text{ in the 50 c.c.}$$

Then $49 : 2{\cdot}459 :: 1000 : 50{\cdot}19$ c.c. = volume of strictly normal acid which contains 2·459 grams of H_2SO_4, and which therefore would be required to neutralise 2·66 grams of sodium carbonate. Hence the acid used is slightly above the normal strength. Its factor, therefore, will be 1·0038; thus—

$$50 : 50{\cdot}19 :: 1 : 1{\cdot}0038$$

(2) The strength of the acid may also be determined gravimetrically by taking 50 c.c. of the acid, and, after diluting with two or three times its volume of water, precipitating it with barium chloride, and proceeding as described in Part I., p. 258.

Normal Sodium Hydroxide.

(40 *grams of* NaHO *per litre.*)

About 45 grams of pure caustic soda, prepared from the metal,* are dissolved in water—which has been recently boiled to expel

* If pure sodium hydroxide is not to hand, it may be prepared by either of the two following methods, namely, (1) by the action of lime upon sodium carbonate, or (2) by the action of sodium upon water.

(1) About 70 grams of sodium carbonate are placed in a clean iron saucepan with 700 c.c. of distilled water, and the mixture heated to boiling. Forty grams of good quicklime are made into a paste with water, and gradually added to the boiling solution, and the mixture boiled until the whole of the carbonic acid in the sodium carbonate is precipitated as calcium carbonate. The completion of the reaction is ascertained by withdrawing a small quantity of the mixture and allowing it to settle in a test-tube. If the sodium carbonate has been wholly converted into caustic, there will be no effervescence when a little of the clear liquid is acidified with a dilute acid. The saucepan is carefully covered, and the contents allowed to settle and become cold. The clear liquid is then decanted off into a stoppered bottle, and a portion of it titrated with standard acid, as described above.

(2) A clean piece of sodium weighing about 25 grams is cut into small pieces, which are introduced one at a time into recently boiled and cooled distilled water in a platinum or nickel dish. A clock-glass should be placed over the dish after the addition of each piece of sodium, in order to prevent the caustic

carbon dioxide, and again cooled—and the volume of the liquid then made up to one litre. Twenty-five cubic centimetres of this solution are then transferred to a small flask by means of a pipette, and titrated with the standard sulphuric acid in the cold, with methyl orange as indicator.

If the caustic soda be free from carbonate, the "end reaction" is very sharply defined when litmus is used as the indicator in the cold; but as the sodium hydroxide, even if free from carbonates to begin with, is always liable to absorb atmospheric carbon dioxide, it is necessary, when employing litmus, to boil off the carbon dioxide during the titration.

From the results obtained, the volume of water which must be added to the solution of caustic soda in order to bring it to normal strength is calculated as explained in the case of the sulphuric acid (p. 320). When this has been done, and the liquid well shaken up to ensure perfect admixture, a fresh titration should be made; and if the alkali is still not absolutely normal, the *factor* is found by which the volume used is to be multiplied in order to make the necessary correction.

The standard sodium hydroxide should be quickly transferred to a store-bottle, the stopper of which is greased with a touch of vaseline; and it should be exposed as little as possible to the air.

Normal Hydrochloric Acid.

(36·5 *grams of* HCl *per litre.*)

The ordinary pure strong hydrochloric acid contains 28 per cent. of HCl; 40 grams, therefore, of the real acid are contained in 143 grams of this solution. Since the specific gravity of this aqueous acid is 1·14, 143 grams will be 125 c.c. This volume, therefore, is measured out into a litre flask, and the volume made up to the 1000 c.c with water at 15°·5.

The actual strength of the acid so obtained is then ascertained by titration with normal sodium hydroxide. Twenty-five cubic

soda from being thrown out in the event of explosions or deflagrations taking place. The process of thus introducing the sodium in fragments which are sufficiently small to render the operation free from danger, is a somewhat long and tedious operation. It may be considerably hastened, however, and the metal exposed much less to the action of atmospheric carbon dioxide, by placing rather more than the requisite quantity of sodium in a sodium wire-press, and slowly squeezing the metal into wire, which is received in water in a nickel or platinum dish. The fine wire of sodium, as it touches the water, fuses at the end, and is rapidly dissolved in the liquid, and the rate at which the wire is driven out can be exactly regulated so that it shall be continuously fed into the water.

centimetres of the alkali are transferred to a small flask, either litmus or methyl orange being used as the indicator, and the acid added from a burette until the point of saturation is reached. From the result obtained, the amount of dilution necessary to bring the acid to normal strength is calculated.

When the acid has been thus corrected, it is once more titrated with the caustic alkali.

As a check upon the result, the acid may be titrated with the normal sodium carbonate, using methyl orange as indicator, and operating in the cold. (Litmus cannot well be used in this case, as the necessary boiling involves loss of hydrochloric acid.)

The exact strength of the acid may also be controlled gravimetrically by precipitating 25 c.c. of the liquid with silver nitrate.

Typical Analyses by means of Standard Acids and Alkalies.

1. **Estimations of the total alkali** in samples of caustic alkali, or in soda-ash ; or determinations of the acid in commercial acids or acid liquids, are conducted in practically the same manner as already described for the titration of the alkalies and acids used for standard solutions. In estimating alkalies containing carbonates, if litmus is employed as indicator instead of methyl orange, the "end reaction" is rendered more certain if a slight excess of the normal acid is run in from the burette, and the mixture boiled to expel the carbon dioxide. The excess of acid is then carefully titrated back with normal caustic soda, which is cautiously added from a burette until one drop restores the blue colour to the litmus. The amount of acid which is represented by the volume of the normal caustic soda thus used, is then deducted from the original total volume of acid employed, which gives the exact amount of acid required to neutralise the alkali under examination.

2. **Estimation of Caustic and Carbonated Alkali in Soda-ash.**—About 5 grams of the soda-ash are weighed into a flask, and dissolved in water, and the solution made up to 250 c.c. Fifty cubic centimetres of this solution are then transferred by means of a pipette to a small flask, and the *total* alkali in it determined by titration with normal sulphuric acid, using either litmus or methyl orange as indicator (see above). The amount of alkali (calculated as Na_2O) contained in 50 c.c. when multiplied by 5 (as only one-fifth of the total was used) gives the amount in the original weight taken, and from this the percentage may be calculated.

Another 50 c.c. of the solution are next transferred to a 100-c.c. flask, and a solution of barium chloride added so long as any

precipitate of barium carbonate is produced.* The liquid is then diluted with water up to 100 c.c. and allowed to settle in the stoppered flask.

Fifty cubic centimetres of the clear solution (equivalent to one-tenth of the original weight taken for the analysis) are withdrawn with a pipette, transferred to a small beaker and titrated with *deci-normal* hydrochloric acid in the cold, with either litmus or methyl orange as indicator. (Sulphuric acid cannot be employed on account of the barium present.)

EXAMPLE.—Weight of soda-ash taken = 5·05 grams.

First Solution.—50 c.c. = one-fifth total soda-ash.

50 c.c. taken and excess of normal sulphuric acid added (1 c.c. = 0·031 gram Na_2O). Volume of acid used... 18·50 c.c.

Titrated back with normal caustic soda (1 c.c. = 1 c.c. normal acid). Volume required ... ... 2·37 „

Hence volume of acid employed in neutralising 50 c.c. soda-ash ... ... 16·13 „

Therefore weight of Na_2O in original weight of soda-ash $= 16{\cdot}13 \times 0{\cdot}031 \times 5 = 2{\cdot}500$ grams

Percentage of Na_2O, or *total alkali* $= \dfrac{2{\cdot}50 \times 100}{5{\cdot}05} = \mathbf{49{\cdot}55}$

Second Solution.—50 c.c. = one-tenth total soda-ash.

50 c.c. taken, and titrated with deci-normal hydrochloric acid (1 c.c. = 0·0031 gram Na_2O). Volume of acid required ... ... 6·3 c.c.

Therefore weight of Na_2O (present as NaHO) in original weight of soda-ash $= 6{\cdot}3 \times 0{\cdot}0031 \times 10 = 0{\cdot}1953$ gram

Hence the percentage of Na_2O present as caustic $= \dfrac{0{\cdot}1953 \times 100}{5{\cdot}05} = \mathbf{3{\cdot}86}$

Then total Na_2O in original weight of soda-ash = 2·500

Na_2O present as caustic alkali = 0·1953

Therefore Na_2O present as carbonated alkali = 2·3047 grams

Hence the percentage of Na_2O present as carbonate $= \dfrac{2{\cdot}3047 \times 100}{5{\cdot}05} = \mathbf{45{\cdot}63}$

* As soon as the whole of the sodium carbonate has been decomposed and the carbonic acid precipitated as barium carbonate, the barium chloride begins to interact with the sodium hydroxide present, forming sodium chloride and barium hydroxide, the latter being equivalent to the sodium hydroxide. The amount of barium chloride used, however, should be as little in excess of that required for the decomposition of the alkaline carbonate as possible, for it is found in practice that when barium hydroxide is produced in any quantity, the results obtained are too low.

The actual percentage of caustic alkali and carbonated alkali may readily be calculated ; thus—

31 : 40 :: 0·1953 = 0·2474 = NaHO equivalent to 0·1953 grams Na_2O

$$\frac{0{\cdot}2474 \times 100}{5{\cdot}05} = \mathbf{4{\cdot}89} = {}^{0}/_{0}\ \mathbf{NaHO}$$

Similarly, 31 : 53 :: 2·3047 = 3·938 = Na_2CO_3 equivalent to 2·3047 grams Na_2O

$$\frac{2{\cdot}3047 \times 100}{5{\cdot}05} = \mathbf{77{\cdot}98} = {}^{0}/_{0}\ \mathbf{Na_2CO_3}$$

Alternative Methods. — (*α*) The soda-ash is dissolved as before, and the total alkali determined in the manner above described. Then a fresh portion (50 c.c.) of the same solution is transferred to a flask, and the whole of the carbonate precipitated by adding barium chloride. Phenolphthalein is then added for the indicator, and the mixture at once titrated with deci-normal hydrochloric acid until the red colour is discharged. The presence of the precipitated barium carbonate does not affect the indicator, and the moment the point is reached when the caustic alkali is neutralised, and the standard acid begins to act upon the barium carbonate, the liberated carbon dioxide discharges the colour of the indicator.

(*β*) In this method the *total* alkali is not first determined. The process depends upon the fact that when sodium carbonate is acted upon by acids, the neutralisation takes place in two stages, so that when half the acid necessary for complete saturation has been added, the carbonate has been converted into the bi-carbonate, which has no power to give a red colour with phenolphthalein. If, therefore, to a mixture of sodium hydroxide and carbonate coloured red with this indicator, normal acid be added, the phenolphthalein will show the point when the *whole* of the caustic soda and *one-half* of the carbonate have become saturated.

Fifty cubic centimetres of the solution prepared as described above is coloured with phenolphthalein, and titrated with normal sulphuric acid. As soon as the colour is discharged, a drop of methyl orange is added, and the titration continued until the yellow liquid becomes pink.

The volume of acid required in the second stage (*i.e.* during the second half of the saturation of the carbonate present) will be one-half of that which has altogether been used up in neutralising the alkaline carbonate. Therefore, if this volume of acid be doubled, and the result subtracted from the total acid used in the whole

process, the difference will represent the volume which was used in saturating the caustic alkali present.

Thus, in the case of the solution of soda-ash used in the first example (containing 5·05 grams in 250 c.c.), 50 c.c. were taken, and titrated with normal sulphuric acid until the phenolphthalein lost its colour.

Volume of acid required	8·7	c.c.
Methyl orange was then added, and the volume of acid required for complete neutralisation	7·45	,,
Total acid used ...	16·15	,,

Therefore acid used in saturating the carbonate } = 7·45 × 2 = 14·90 c.c.

and acid used in saturating the caustic alkali } = 16·15 − 14·90 = 1·25 c.c.

These, when calculated as percentages, as in the former example, give—

Percentage carbonate = 78·1
Percentage caustic = 4·9

3. **Estimation of Ammonia.**

(*a*) *Direct Method.*—A solution of the ammonium salt in water is boiled with a solution of caustic soda, and the ammonia thus expelled is absorbed in a measured volume of normal sulphuric acid. The *excess* of acid is then ascertained by titration with normal sodium hydroxide; and by deducting this excess from the total volume of acid employed, the volume of acid which has been saturated by the ammonia is found, and from this the weight of ammonia is calculated.

From 1 to 2 grams of ammonium chloride are weighed out into the flask F (Fig. 53, p. 250), and dissolved by the addition of a small quantity (40 to 50 c.c.) of water. One hundred cubic centimetres of normal sulphuric acid are run into the absorption flask through the scrubber-tube, and the process of distilling and absorbing the ammonia is carried out exactly as described on p. 251.

After the whole of the ammonia has been expelled, the apparatus is disconnected, and the end of the leading tube and the contents of the scrubber-tube are thoroughly rinsed into the flask, so as to wash out of the latter every trace of the acid with which the broken glass was moistened. A few drops of methyl orange are then added, and the liquid titrated with normal caustic soda.

The quantity of acid which is equivalent to the volume of the normal soda required for neutralisation, is the *excess* which has

remained over after the whole of the ammonia has been saturated. On deducting this from the total volume of acid used (namely, 100 c.c.), the actual amount of acid neutralised by the ammonia is found, and by calculation the weight of ammonia, NH_3 (or of ammonium, NH_4), is ascertained.

(*b*) *Indirect Method.*—In this method the weighed quantity of ammonium salt is boiled with a measured volume of normal sodium hydroxide, until the ammonia is all expelled. A certain quantity of the soda is thus decomposed, being converted into the sodium salt of the acid which was in combination with the ammonia. For example, supposing the ammonium salt to have been the sulphate—

$$(NH_4)_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O + 2NH_3$$

If, when the whole of the ammonia has been expelled, the remaining undecomposed caustic soda be determined by means of normal acid, the amount of soda which has been used up in expelling the ammonia will be found ; and from this the quantity of ammonia so displaced can be calculated.

About 2 grams of pure ammonium sulphate are weighed out into a small flask, and 30 c.c. of normal caustic soda added. The mixture is then boiled until the escaping steam produces no brown stain upon a strip of turmeric paper. Three or four drops of litmus solution are then added, and the liquid titrated with normal sulphuric acid. The volume of normal soda equivalent to the number of cubic centimetres of acid used to produce neutrality, when deducted from the total volume of soda employed (namely, 30 c.c.) gives the number of cubic centimetres of soda which were decomposed in the process of expelling the ammonia.

From the above equation, it is seen that 40 grams of caustic soda are used up in the expulsion of 17 grams of ammonia ; therefore each cubic centimetre of normal soda (0·040 gram) is equivalent to 0·017 gram of ammonia, NH_3.

4. **Estimation of the "Hardness" of Water*** (Hehner's method).

(*a*) *Temporary hardness* (due to the presence of calcium or magnesium carbonate) is determined by means of standard sulphuric acid of one-fiftieth normal strength. This is prepared by diluting 20 c.c. of the normal acid up to 1000 c.c. with water. One cubic centimetre of this acid is equivalent to 0·001 gram $CaCO_3$.

One hundred cubic centimetres of the water to be examined are transferred to a beaker, and 3 drops of methyl orange added.

* For Clark's soap-test for hardness in water, see Precipitation methods, p. 371.

The $\frac{N}{50}$ sulphuric acid is then delivered from a burette until the solution becomes red.

Each cubic centimetre of acid represents 1 milligram of $CaCO_3$ in 100 c.c. of water; therefore it also stands for parts per 100,000. *E.g.* suppose 13 c.c. of acid were required to exactly neutralise the carbonate; then 100 c.c. of the water contain 0·013 gram of $CaCO_3$; or its equivalent of $MgCO_2$, and 100,000 parts contain 13 parts of $CaCO_3$ (or the equivalent of $MgCO_3$).

One part of $CaCO_3$ per 100,000 of water is termed 1 degree of hardness; hence the water in question has a temporary hardness of 13 degrees.

(*b*) *Permanent hardness* (due mainly to the presence of calcium or magnesium sulphate) is estimated by means of standard sodium carbonate of one-fiftieth the normal strength (prepared by diluting 20 c.c. of the normal solution to 1 litre with water). One cubic centimetre of this solution will precipitate 0·001 gram $CaCO_3$. Excess of this is added to the water, which is then evaporated to dryness. The residue is treated with water, and after removing the precipitated carbonates by filtration, the excess of sodium carbonate is determined by means of $\frac{N}{50}$ sulphuric acid.

One hundred cubic centimetres of the water are transferred to a platinum dish, and a measured volume of the $\frac{N}{50}$ sodium carbonate —considerably in excess of that required for complete precipitation —is added. The solution is then evaporated to dryness on a steam bath. The residue is taken up with water and filtered, the dish and filter being thoroughly washed. The sodium carbonate in the liquid is then determined by titration with the $\frac{N}{50}$ sulphuric acid. The excess of sodium carbonate thus found, deducted from the total volume added, gives the number of cubic centimetres used in removing the permanent hardness. Each cubic centimetre so employed represents 0·001 gram of calcium carbonate (formed from the sulphate *) precipitated from 100 c.c. of water; it therefore also represents parts per 100,000.

* From the following equations, it will be seen that, although sodium carbonate precipitates calcium carbonate from the soluble bicarbonate of lime (temporary hardness) as well as from the sulphate (permanent hardness)—that, in other words, it removes both temporary and permanent hardness—it is only in decomposing the sulphate that the alkali is destroyed. In the other case the solution contains the equivalent of sodium bicarbonate—

$$H_2CO_3.CaCO_3 + Na_2CO_3 = CaCO_3 + 2HNaCO_3$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

For example, 100 c.c. of the water were taken, and 50 c.c. of $\frac{N}{50}$ sodium carbonate added. After evaporating to dryness and extracting with water, the solution required 41 c.c. of $\frac{N}{50}$ sulphuric acid to neutralise it. $50 - 41 = 9$, therefore 9 c.c. of the sodium carbonate were used up in removing the permanent hardness, hence the water contained 9 degrees of permanent hardness. The temporary hardness added to the permanent hardness gives the *total* hardness of the water.

SECTION III.

Volumetric Methods based upon Oxidation and Reduction.

In the various processes which are included in this section, there is always an oxidising agent (in other words, a *reducible* substance) and an oxidisable body, *i.e.* a reducing agent.

Sometimes the *oxidising material* is the standard reagent, which, by its own reduction, furnishes the measure of the amount of the oxidisable substance which is present. Thus, the reduction of a known volume of standard potassium permanganate, or potassium dichromate, will afford a measure of the quantity of iron which has been oxidised from the ferrous to the ferric condition; the ferrous salt in this case being the oxidisable substance, or the reducing agent.

In other cases the standard reagent is the *reducing agent*, which undergoes oxidation at the expense of some oxidising (*i.e.* reducible) compound present, and thereby affords the means of estimating the amount of such a substance. Thus, the oxidation of a known volume of standard sodium arsenite into arsenate, may become the measure of the amount of chlorine present in bleaching powder; or of the quantity of free iodine in a solution. The chlorine or the iodine in this case is the oxidising agent, not by *directly* giving oxygen, as in the case of potassium permanganate, but by *indirect* oxidation through the intervention of water; the hydrogen of which is taken by the halogen, while an equivalent of oxygen is liberated.

The most important of the oxidising standard solutions are potassium permanganate, potassium dichromate, and iodine; while the reducing compounds in commonest use are ferrous salts, oxalic acid, sodium thiosulphate, sodium arsenite.

Deci-normal Potassium Permanganate.

(3·16 *grams of* $KMnO_4$ *per litre.**)

3·16 grams of the purest recrystallised and dry salt† are weighed out and dissolved in water in a litre flask, and the solution made up to 1000 c.c. with water at 15°.

Solutions of potassium permanganate slowly undergo decomposition by light; if, therefore, the solution is to be kept for any length of time, it is preferably transferred, either to a deep-blue bottle, or to one covered with black paper, and kept in a cupboard. The solution must not be allowed to come in contact with any organic matter; on this account, burettes with glass taps must always be employed for this reagent.

Titration of Deci-normal Permanganate.—(*a*) *By means of Ferrous Sulphate—*

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$$

or, expressing only the relation between the available oxygen and the ferrous oxide—

$$5O + 10FeO = 5Fe_2O_3$$

The deci-normal solution being one-tenth of the strength of the normal solution—which, in its turn, contains (in the case of permanganate) only one-tenth of the formula-weight of the salt per litre—will contain 0·0008 gram of available oxygen per cubic centimetre; or each cubic centimetre will be equivalent to 0·0056 gram of iron in the ferrous state; *i.e.* it will be capable of oxidising this weight of iron from the *ferrous* to the *ferric* condition.

For the purposes of this titration, the ferrous sulphate is prepared by dissolving 0·5 gram of the purest soft iron wire in sulphuric acid, with exclusion of air, the wire being clean and free from rust.‡

About 80 c.c. of dilute sulphuric acid (1 part acid to 5 parts water) are placed in a 250-c.c. flask fitted with a rubber cork and bent glass tube. The air in the flask is then expelled by removing the cork and introducing two or three crystals of pure sodium carbonate, the flask being in a vertical position. As soon as the carbonate has dissolved, the weighed quantity of iron is dropped

* See p. 314.

† If the ordinary "pure" commercial salt be used, about 3·2 to 3·5 grams should be taken.

‡ The fine iron binding wire used for flowers is the best for the purpose; it contains 99·6 per cent. of iron.

in. The cork is then inserted, and the flask supported in the manner shown in Fig. 72, with the tube dipping into a solution of sodium carbonate in a small beaker. The flask being in this inclined position, the fine spray thrown up during the solution of the iron strikes against the sides of the flask and falls back into the liquid. The flask is gently heated by means of a small flame until the iron is wholly dissolved, and only a few minute particles of carbon remain. The lamp is then withdrawn, and the flask allowed to cool. As it does so, the solution in the beaker is gradually drawn up the tube, but the first drops which enter the flask at once cause an effervescence of carbon dioxide which drives the liquid down again, and at the same time fills the flask with carbon dioxide. When it has partially cooled in this way, the cork is removed, and air-free distilled water (prepared by boiling the water, and again quickly cooling it) is added until the solution is within about 20 or 30 c.c. of the graduation mark. The flask is then closed with a rubber stopper, and the contents made quite cold by holding the vessel in a stream of cold water. The solution is then made up to 250 c.c. by the further addition of cold air-free water.

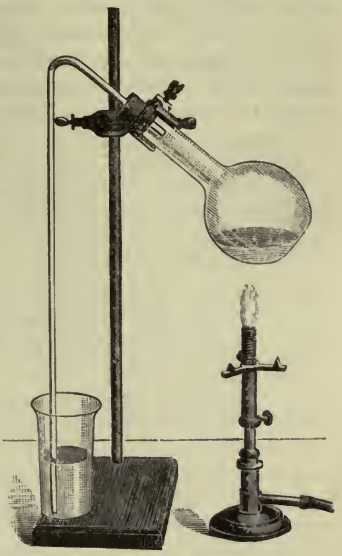

Fig. 72.

Fifty cubic centimetres of this solution are transferred by means of a pipette to a small flask, and diluted by the addition of about half the volume of air-free distilled water. The flask is placed upon a white tile, and the deci-normal permanganate solution added from a burette until the colour of the reagent ceases to be destroyed, and a faint pink tint is imparted to the solution.

Four separate experiments should be made, taking 50 c.c. of the iron solution each time, in order to gain practice in judging when the first appearance of the permanent pink colour takes place. After the experience thus gained, in subsequent duplicate titrations the volume of the reagent used should agree to 0·1 of a cubic

centimetre. From the results obtained, the exact strength of the permanganate is calculated; thus—

0·5 gram of iron wire was dissolved in 250 c.c. of liquid. Fifty cubic centimetres of the solution therefore contain 0·1 gram of iron. But since the iron wire contained 99·60 per cent. of iron, the actual weight of iron present is found by multiplying the weight of the wire by 0·996. Hence 50 c.c. of the solution contain not 0·1 gram, but 0·0996 grams of iron. Three titrations were made, which required respectively 17·64 c.c., 17·74 c.c., and 17·70 c.c. of the permanganate, or 17·69 as a mean figure.

Then 17·69 c.c. : 1 c.c. :: 0·0996 gram : 0·00563 gram

Therefore the solution is very slightly stronger than the exact deci-normal, since 1 c.c. should be equivalent to 0·0056 gram of iron.

(*b*) *Titration of Permanganate with Ferrous Ammonium Sulphate*, $FeSO_4,(NH_4)_2SO_4,6H_2O$.—The formula-weight of this salt (392) is exactly seven times the weight of the iron it contains (56); hence in 3·5 grams of the compound there will be 0·5 gram of iron.

Exactly 3·5 grams of the pure salt are weighed out and dissolved in air-free water, and the solution made up to 250 c.c. Fifty cubic centimetres of this solution, therefore, will contain 0·1 gram of iron. For the titration, 50 c.c. of the solution are transferred to a small flask, and 10 or 15 c.c. of dilute sulphuric acid added. The deci-normal solution is then run in, as in the former case, until the pink colour persists.

(*c*) *Titration of Permanganate with Oxalic Acid*, $H_2C_2O_4,2H_2O$.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$$\text{or } 5O + 5H_2C_2O_4 = 5H_2O + 10CO_2$$

Hence 8 parts of oxygen (1 equivalent) is capable of oxidising 45 parts of oxalic acid (calculated as anhydrous), or 63 parts of the crystallised compound. Therefore 1 c.c. of the deci-normal permanganate, which is equivalent to 0·0056 gram of iron, will be equivalent also to 0·0063 gram of crystallised oxalic acid.

6·3 grams of recrystallised and dry * oxalic acid are weighed out, dissolved in water, and the solution diluted to 1 litre. The solution so obtained is deci-normal oxalic acid; but, in order to make sure that the acid is pure, and of the exact state of hydration represented by the formula $C_2H_2O_4,2H_2O$, the precise strength of the

* The term *dry* signifies freedom from adherent moisture, and does not refer to the anhydrous compound.

solution should be determined by titration with a deci-normal caustic alkali, using phenolphthalein as indicator.

Twenty-five cubic centimetres of the deci-normal oxalic acid are transferred to a small flask, and about half the volume of dilute sulphuric acid added.* The mixture is then gently heated to a temperature from 50° to 60°, and the permanganate solution slowly run in from a burette. In this reaction the discharge of the colour of the permanganate is not so instantaneous as in the case of the ferrous compounds, there being an intermediate formation of a brown colour, which then fades away, leaving the liquid colourless. Hence it is necessary to add the permanganate cautiously, especially as the end of the reaction approaches, in order that the first signs of the permanent pink colour may be detected. Two or three titrations should be made (using various quantities of the deci-normal oxalic acid) for practice in observing the end reaction.

If the oxalic acid be strictly deci-normal (as determined by means of deci-normal alkali), and the permanganate be likewise exact, 25 c.c. of the acid should require 25 c.c. of permanganate.†

Typical Analyses by means of Potassium Permanganate.

(1) **Estimation of Iron in Iron Ores.**‡—If the iron is present in the *ferrous* state, the substance is dissolved with careful exclusion of air, and the solution titrated as already described. If the iron is in the *ferric* condition, it is reduced (after solution) by the method given below. When the metal is present partly as *ferrous* and partly as *ferric* iron, the *ferrous* iron is first estimated in one portion, and a second portion is then subjected to the reducing agent, and the *total* amount of iron determined. The difference between the two results represents the iron which existed in the ferric state.

(*a*) *Iron in the Ferrous State.*—About 0·5 gram of spathic iron ore, in the *finest possible powder*, is weighed out and dissolved in

* The presence of acid (preferably sulphuric acid) is necessary in all titrations with potassium permanganate, in order to keep the manganous oxide in solution. Nitric and hydrochloric acids are prejudicial; with the latter acid (unless present only in small quantities and the liquid is cold), chlorine is liberated by the oxidising action of the permanganate.

† Dilute solutions of oxalic acid, such as the deci-normal, are liable to undergo decomposition if preserved; hence, if the solution has been prepared any length of time, it should be retitrated with alkali before being used.

‡ Such as *magnetic oxide*, *red* or *brown hæmatite*, *clay ironstone*, *spathose*, *black band*.

20 c.c. of a mixture of equal volumes of strong hydrochloric acid and water, with exclusion of air, in the apparatus described on p. 333.* The acid is gently boiled by means of a small flame until the iron is entirely extracted. The solution is then largely diluted by adding 100 c.c. of cold air-free water, and at once titrated by means of deci-normal permanganate.†

(*b*) *Total Iron.*—A second portion of ore, about 0·5 gram, is weighed out and dissolved in a similar quantity of acid. The operation may be conducted in a flask supported as shown in Fig. 72, but the cork with the leading tube may be removed.

When the solution of the ore is complete, the liquid is considerably diluted with water, and about 15 c.c. of strong sulphuric acid added. A few fragments of pure zinc (*i.e.* free from iron‡) are then introduced into the flask, and the cork with its leading tube is inserted. Hydrogen is evolved by the solution of the zinc in the acid liquid, and the iron existing in the *ferric* state is thereby reduced to the *ferrous* condition. The action is allowed to continue *until the zinc is entirely dissolved*, the process being aided towards the end by the application of heat. In order to test whether the reduction of the iron is complete, a drop of the liquid is withdrawn upon the end of a fine glass rod, and brought into contact with a drop of a solution of ammonium thiocyanate upon a white tile.

Any remaining ferric salt will be revealed by the formation of the red colour; in which case the process must be continued by the addition of more zinc, and, if necessary, of more acid also. When the iron is entirely in the ferrous state, the solution is quickly cooled, and then titrated with the permanganate.

By deducting the amount of iron present as *ferrous* iron from the total iron in the ore, the amount of iron which is in the ferric state is ascertained.

* In the case of the carbonate of iron, the carbon dioxide evolved will serve to displace the air without the addition of sodium carbonate.

† It is very necessary that the amount of hydrochloric acid present should be quite small, and the solution cold and dilute, otherwise the analysis will be vitiated by the action of the acid upon the permanganate, whereby chlorine is liberated; thus—

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl$$

‡ If *pure* zinc is not available, the zinc that is employed must be weighed before being introduced, and the amount of iron present must be found by dissolving a similar quantity of the zinc in acid, and titrating with permanganate. Or magnesium may be used instead of zinc. Other methods by which iron may be reduced, but which are more applicable when the titration is to be made with potassium dichromate, are described on pp. 343, 344.

EXAMPLE.—0·5 gram of spathic iron ore.

(*a*) *Ferrous Iron.*

Permanganate required ... ... 34·4 c.c.

(1 c.c. = 0·0056 Fe, = 0·0072 FeO, = 0·0080 Fe_2O_3)

Then 34·4 × 0·0072 = 0·24768 = weight of FeO

and $\frac{0·24768 \times 100}{0·5}$ = **49·53** = per cent. of FeO in the ore

(*b*) *Ferric Iron.*—0·5 gram of ore.

Permanganate required ... ... 36·6 c.c.

Deducting the volume used in the first titration ... ... 34·4 „

Gives the volume required for the iron present in the *ferric* state ... ... 2·2 „

But the zinc used contained 0·08 per cent. of iron. Five grams were employed; therefore $\frac{0·08 \times 5}{100}$ = 0·004 gram of iron which was introduced.

The volume of permanganate used in oxidising this quantity of iron is 0·0056 : 0·0040 :: 1 : 0·71 c.c. 2·2

0·71

Deducting this, gives the true volume of permanganate required for the iron originally present as *ferric* iron 1·49 c.c.

Then 1·49 × 0·0080 = 0·01192 = weight of Fe_2O_3

and $\frac{0·01192 \times 100}{5}$ = **2·38** = per cent. of Fe_2O_3 in the ore

(2) **Estimation of Available Oxygen in Manganese Ores.**—The available oxygen in a manganese ore is that oxygen which can be made use of for oxidising purposes when the ore is decomposed by an acid. Thus, in the sesquioxide one-third, and in the dioxide one-half, of the total oxygen is available for this purpose. When acted upon by sulphuric acid, this oxygen is evolved as such; thus—

$$Mn_2O_3 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O$$
$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

while, when decomposed by hydrochloric acid, chlorine is evolved, in each case in quantity equivalent to the oxygen—

$$Mn_2O_3 + 6HCl = 2MnCl_2 + 3H_2O + Cl_2$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

Methods for valuing manganese ores are based upon both of

these reactions. In the first case the evolved oxygen is used in oxidising either a ferrous salt or oxalic acid ; while in the second, the chlorine is made to liberate its equivalent of iodine, which is then determined by means of sodium thiosulphate.

In this place, examples based upon the first reaction are given ; the second method is described on p. 356.

(*a*) *By the Oxidation of Ferrous Sulphate.*

$$MnO_2 + 2H_2SO_4 + 2FeSO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$

That is to say, 1 atom or 16 parts of oxygen (which is the representative of 1 equivalent (or 87 parts) of manganese dioxide), will oxidise 2 atoms or 112 parts of ferrous iron.

If, therefore, manganese dioxide be dissolved in sulphuric acid, in the presence of a known quantity of ferrous salt (which must be in excess), every 8 parts of oxygen, or 43·5 parts of MnO_2 will oxidise 56 parts of Fe ; and if the amount of ferrous salt which remains unoxidised be then determined by means of deci-normal permanganate, the quantity of iron oxidised, and therefore the amount of manganese dioxide, can be calculated.

About 1 gram of soft iron wire is weighed out and dissolved in about 40 c.c. of dilute sulphuric acid (1 part acid to 4 parts water) in the apparatus shown on p. 333.

As soon as it is completely dissolved, 0·75 to 1 gram of finely powdered pyrolusite, previously dried at 100°, is introduced into the flask, and the cork with its tube replaced. The mixture is gently heated until the ore has entirely dissolved, or until all visible black particles have disappeared. The solution is cooled in the manner described on p. 333, diluted with air-free water, and the excess of ferrous salt titrated with permanganate.

The excess of unoxidised iron thus found, deducted from the weight of iron taken, gives the quantity of iron which has been oxidised by the manganese dioxide ; and from this, by the equation given above, the percentage of available oxygen—either as *oxygen*, or in terms of *manganese dioxide*—can be calculated. Thus—

Volume of permanganate (1 c.c. = 0·0056 Fe) required } = 22·4 c.c.

22·4 × 0·0056 = 0·125 gram = excess of Fe

1 gram iron wire (99·6 per cent. of Fe) } = 0·996 gram = total iron taken

therefore 0·996 − 0·125 = 0·871 gram = iron oxidised by 0·75 gram of the ore

$$\overset{Fe}{56} : \overset{Fe}{0{\cdot}871} :: \overset{MnO_2}{43{\cdot}5} : 0{\cdot}6765 \text{ gram } MnO_2$$

$$\text{and } \frac{0{\cdot}6765 \times 100}{0{\cdot}75} = \mathbf{90{\cdot}0} = \textbf{percentage of } \mathbf{MnO_2} \textbf{ in the ore}$$

(*b*) *By the Oxidation of Oxalic Acid*—

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2CO_2 + 2H_2O$$

Hence every 8 parts of oxygen, or 43·5 parts of MnO_2, will oxidise 63 parts of crystallised oxalic acid. About 0·25 gram of the manganese ore is weighed into a flask, and 10 c.c. of normal oxalic acid added. Twenty-five cubic centimetres of dilute sulphuric acid (1 part acid to 4 parts water) are added, and the mixture gently warmed until the decomposition is complete and no black particles are visible. The solution is then cooled, and made up to 100 c.c. with cold water. The excess of oxalic acid remaining is titrated with deci-normal permanganate, taking 25 c.c. of the solution. The amount of oxalic acid thus found, deducted from the total employed, gives the quantity which has been oxidised by the manganese ore, from which the percentage of available oxygen or of manganese dioxide can be calculated. For example, after acting upon 0·25 gram of pyrolusite—

25 c.c. of the solution required of permanganate (1 c.c. = 0·0063 gram oxalic acid) ... ... 12·1 c.c.
Multiplying by 4 gives for the total excess of oxalic acid 48·4 „

48·4 × 0·0063 = weight of oxalic acid in excess = 0·3049 gram

Weight of oxalic acid in 10 c.c. normal solution... 0·63
Deducting the excess ... ... 0·3049

Gives the weight of oxalic acid oxidised by the ore 0·3251

Then 63 : 0·3251 :: 43·5 = 0·223 = weight of MnO_2

$$\text{and } \frac{0{\cdot}223 \times 100}{0{\cdot}25} = \mathbf{89{\cdot}2} = \text{percentage of } MnO_2$$

(3) **Estimation of Tin.**—When stannous chloride is mixed with ferric chloride, or when metallic tin is dissolved in ferric chloride mixed with hydrochloric acid, the stannous chloride is oxidised to stannic chloride at the expense of the ferric chloride. A quantity of ferrous iron, equivalent to the weight of tin, is thus formed in the solution according to the equation—

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2$$

Every 56 parts of iron converted into the ferrous state, therefore, is equivalent to 59 parts of tin. The amount of ferrous salt so produced is titrated by means of potassium permanganate.

About 0·5 gram of granulated tin is weighed into a 250-c.c. flask, and a few cubic centimetres of a moderately strong solution of ferric chloride, together with a little hydrochloric acid, are added. A crystal of sodium carbonate is dropped into the mixture in order to replace the air with carbon dioxide, and the flask loosely corked and gently warmed. When the tin has wholly dissolved, the solution (still yellow with excess of ferric chloride) is diluted up to 250 c.c. with cold air-free water. Fifty cubic centimetres of this liquid are then withdrawn by means of a pipette, and titrated with deci-normal permanganate.*

(4) **Estimation of Calcium.**

(*a*) The calcium is precipitated in the form of calcium oxalate by means of ammonium oxalate, in the manner described for the gravimetric estimation, p. 231. The precipitate, after being thoroughly washed to remove every trace of ammonium oxalate, is dissolved in a small quantity of warm hydrochloric acid, and the solution diluted with water. Sulphuric acid is then added, and the mixture heated to between 60° and 70°, and the free oxalic acid titrated by means of permanganate. Sixty-three parts of oxalic acid found, are equivalent to 20 parts of calcium; or 1 c.c. $\frac{N}{10}$ permanganate, which is equal to 0·0063 gram oxalic acid, represents 0·002 gram of calcium.

About 0·5 gram of marble or limestone is weighed out, and dissolved and precipitated by means of ammonium oxalate in the manner described on p. 231. The perfectly washed precipitate is then washed into a flask by thrusting a glass rod through the apex of the filter, and that which remains adhering to the paper is dissolved off by treating it with a little warm hydrochloric acid. The filter is thoroughly rinsed with water, and if the whole of the precipitate in the flask is not dissolved, a few more drops of acid are added, avoiding unnecessary excess. A few cubic centimetres of strong sulphuric acid are now added, and the solution made up to 250 c.c. Fifty cubic centimetres of this solution are then withdrawn, and gently warmed to a temperature about 60°, and then titrated with deci-normal permanganate.†

* A method for estimating copper is based upon a similar reaction. The copper is first reduced either to cuprous oxide by means of grape sugar, or to the metallic state by means of pure metallic zinc, and the reduced product is then dissolved in a mixture of ferric chloride and hydrochloric acid—

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + H_2O + 2FeCl_2$$
$$Cu + Fe_2Cl_6 = CuCl_2 + 2FeCl_2$$

† Other metals (*e.g.* lead) which admit of complete precipitation in the form of oxalates or basic oxalates (bismuth) are capable of being estimated on

(*b*) Instead of determining the oxalic acid which is actually in combination with the calcium, the calcium may be precipitated by means of an excess of a standard oxalic acid solution, and after removing the precipitate by filtration, the excess of oxalic acid is found by means of permanganate. By deducting this excess from the total amount used, the quantity of oxalic acid which was precipitated by the calcium is found, and from this the percentage of calcium is calculated.

About 0·5 gram of calc-spar is weighed out, and dissolved in dilute hydrochloric acid in a flask. Twenty cubic centimetres of normal oxalic acid (63 grams per litre) are delivered into the flask, and a slight excess of ammonia added. The mixture is boiled for a few minutes, and then allowed to cool, after which it is diluted with water up to 250 c.c. The liquid is then filtered through an *unwetted* filter, and when sufficient has passed through, 50 c.c. of the perfectly clear filtrate* are withdrawn with a pipette and transferred to a small flask, in which the solution is acidified with sulphuric acid, heated to about 60°, and titrated with deci-normal permanganate.

Since one-fifth of the total solution was used for the titration, the result multiplied by 5 will give the excess of oxalic acid; and this deducted from the original quantity taken will give the amount which was precipitated as calcium oxalate.

Deci-normal Potassium Dichromate.

(4·913 *grams per litre.*†)

4·913 grams of pure potassium dichromate (previously dried by being gently fused in a porcelain dish, and then powdered in a dry mortar) are exactly weighed out and dissolved in water in a litre flask, and the solution made up to 1000 c.c. with water at 15°.

One litre of this $\frac{N}{10}$ solution contains one-tenth of an equivalent of available oxygen in grams, *i.e.* 0·8 gram; hence 1 c.c. = 0·0008 gram available oxygen, and is equivalent to 0·0056 Fe, or to the one-thousandth of the equivalent weight of any substance capable of being fully oxidised by one equivalent of oxygen.

Unlike potassium permanganate, the dichromate solution is

this principle. Thus zinc and cadmium oxalates also are completely precipitated by oxalic acid on the addition of a moderate quantity of alcohol. Alkali salts must be absent, as these produce soluble double oxalates.

* Any calcium oxalate passing through the filter will be subsequently decomposed by the acid, and will be therefore returned as excess oxalic acid, and so vitiate the analysis.

† See p. 313.

stable, and as it has no action upon rubber, it may be used in a burette which is closed by a rubber tube and pinchcock.

Titration of Decinormal Potassium Dichromate.

(*a*) *By means of Ferrous Sulphate*—

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

or, since the dichromate contains 3 atoms of available oxygen, the reaction may be expressed—

$$3O + 6FeO = 3Fe_2O_3$$

For the purposes of the titration, the ferrous sulphate is prepared by dissolving pure iron in dilute sulphuric acid, with exclusion of air, precisely as described for permanganate, p. 333. An aliquot part of the solution—say 50 c.c.—is withdrawn by means of a pipette, and transferred to a small flask, and the dichromate solution gradually added from a burette.

In this process, the end of the reaction is ascertained by means of a freshly made and dilute solution of potassium ferricyanide, used as an *outside* indicator. A number of drops of the ferricyanide are placed about upon a white plate or tile, and from time to time, during the addition of the dichromate, a drop of the mixture is withdrawn upon a glass rod and brought into contact with one of the drops of the indicator. At first a strong blue coloration is produced, but as the amount of ferrous salt is gradually diminished by the addition of the dichromate, the blue becomes less and less intense, until at last a drop of the liquid so tested fails to give any coloration. At this point the whole of the ferrous salt has been oxidised, and the reaction is therefore complete.*

(*b*) *By means of Ferrous Ammonium Sulphate.*—The process is carried out as in the case of potassium permanganate, the end reaction being determined by means of ferricyanide, as described above.

Analyses by means of Potassium Dichromate.

In a number of instances, potassium dichromate may be substituted for permanganate in volumetric analysis. This is the case, for example, with all estimations that are based upon the oxidation of ferrous to ferric salts; but not with those in which oxidation of oxalic acid is the foundation of the process.

* It will be evident that it is absolutely essential to the success of this operation that the ferricyanide should be perfectly free from ferrocyanide, otherwise the oxidised iron will itself give rise to a blue coloration.

The precautions as to the presence of hydrochloric acid, which have to be taken when using potassium permanganate, do not apply in the case of the dichromate; and the solution to be titrated may be less dilute when the latter reagent is employed.

The reducing agent to be used, in order to convert the iron into the ferrous state previous to titration with potassium dichromate, is either an alkaline sulphite, or stannous chloride. Reduction by means of metallic zinc (which is the method most suitable when permanganate is to be used, see p. 336) is not so well adapted for solutions which are to be titrated with the dichromate solution, as the presence of the dissolved zinc salt interferes with the reaction with the ferricyanide indicator.

(1) **Estimation of Iron in Iron Ores.***—About 1 gram of finely powdered and dry red hæmatite is weighed out into a flask and boiled with a small quantity of strong hydrochloric acid, diluted with about half its own volume of water, until the whole of the iron has been extracted,† and the residue is free from dark-coloured particles.

Reduction by means of Stannous Chloride.—The solution is cooled and diluted up to 100 c.c. with cold water. Twenty-five cubic centimetres of this solution are then transferred to a small flask by means of a pipette, and heated to the boiling-point over a small flame. A clear freshly prepared solution of stannous chloride is cautiously added, drop by drop, until the yellow colour of the ferric chloride is just discharged, carefully avoiding *unnecessary excess*—

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2$$

The slight excess of stannous chloride is removed from the solution (as stannous chloride is oxidised by potassium dichromate, and its presence, therefore, would vitiate the subsequent titration), by adding a few drops of a solution of mercuric chloride, whereby

* In the example here given, the *total* iron is alone estimated. When the amount of ferrous and ferric oxide present is to be separately determined, the procedure is the same as that described on p. 335; the reduction of the iron in the second portion (in which the total iron is estimated) is accomplished either by stannous chloride or alkaline sulphite, and the solutions titrated with dichromate.

† In cases where the iron is difficult to extract with hydrochloric acid alone, a few small crystals of potassium chlorate may be added, after which the solution must be evaporated to dryness, and the residue dissolved in hydrochloric acid. Iron ores (such as the titaniferous ores) from which the iron cannot be wholly extracted by acids, are mixed in a state of fine powder with from 6 to 10 times their weight of hydrogen potassium sulphate (*bisulphate of potash*), and gently fused in a platinum dish for from 20 to 30 minutes. The "melt" is extracted with dilute hydrochloric acid.

mercur*ous* chloride is precipitated (which is without action upon the dichromate), and stannic chloride produced *—

$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4$$

The solution is now titrated with the deci-normal dichromate without unnecessary exposure to the air. The volume of the dichromate used, multiplied by 4 (as 25 c.c. out of the 100 c.c. were used for the titration), gives the volume required to oxidise the iron in the original weight of ore taken.

Reduction by means of Alkaline Sulphite.—The solution of the ore obtained by boiling with hydrochloric acid is slightly diluted, and, if necessary, filtered through a small filter into a flask, the filter and residue being thoroughly washed. Ammonia is added to the liquid until slightly alkaline, as shown by the formation of a faint permanent precipitate of ferric hydroxide. One or two drops of dilute hydrochloric acid are then added, in order to *just* re-dissolve this precipitate.

Ten cubic centimetres of a strong solution of hydrogen ammonium sulphite † (ammonium bisulphite), $H(NH_4)SO_3$, are then added, and thoroughly mixed by shaking, and the solution gradually heated to boiling. Ten cubic centimetres of strong sulphuric acid are mixed with an equal volume of water, and this mixture is added to the heated liquid, and the boiling continued for 15 or 20 minutes to expel the whole of the sulphur dioxide. The solution is then cooled quickly and diluted to 100 c.c. with cold water. Twenty-five cubic centimetres of this are then titrated with the deci-normal dichromate.

(2) **Estimation of Chromium in Chrome Iron Ore.**

By the exact converse of the foregoing process, chromium (in the condition of chromate) is most readily estimated. In the case of chrome iron ores (as also with ferro-chromium), the chromium is converted into sodium chromate by fusion with sodium peroxide. The chromate is then reduced by means of a measured or weighed excess of a ferrous salt, and the excess of the latter then estimated by titration with deci-normal dichromate solution.

* If no precipitate is produced on the addition of the mercuric chloride, it shows that an insufficient quantity of stannous chloride was added. Too copious a precipitate, due to too great an excess of the tin solution, will interfere with the titration.

† That is to say, about 1 c.c. for each 0·1 gram of ore which was dissolved. The bisulphite may be prepared by passing a gentle stream of sulphur dioxide through a small quantity of strong ammonia solution, diluted with half its volume of water. The ammonia may be contained in a boiling-tube, which is kept cool by being immersed in a beaker of cold water. The gas is bubbled through it until the liquid smells strongly of sulphur dioxide, and until the crystals of the normal sulphite which first form are wholly re-dissolved.

About 0·5 gram of the *finely powdered* ore * is weighed out into a nickle crucible † and intimately mixed with 3 to 4 grams of sodium peroxide. The crucible is then heated by means of a Bunsen flame, and the mixture kept in a state of fusion for 5 to 10 minutes It is then allowed to partially cool, until a crust is formed upon the surface of the fused mass, when 1 gram of sodium peroxide is added, and the materials again melted and kept in a state of fusion for 5 minutes longer.

After cooling, the crucible is transferred to a porcelain beaker (or, in the absence of this, a porcelain dish), and the melt exhausted with hot water, the beaker or dish being covered with a clock-glass. The solution is then boiled for 10 minutes, in order to decompose completely the whole of the remaining sodium peroxide.‡ [Should the solution first obtained by dissolving the melt be purple in colour, due to sodium ferrate, a little more sodium peroxide should be added before boiling the liquid.]

The iron present in the ore (the manganese, in the case of ferro-chromium), and the nickel derived from the crucible, are left in the form of oxides, which are separated by filtering and carefully washing the residue upon the filter. The yellow solution containing the chromium, as sodium chromate, is acidulated with sulphuric acid, and an excess of ferrous ammonium sulphate added. This is most conveniently done by adding a weighed quantity of the solid salt. A weighing-bottle, filled with the salt, is first weighed, and then small quantities are carefully taken out upon a small clean spatula (holding the bottle over the beaker containing the chromate solution, lest any particles should fall), and added to the liquid until the chromium is entirely reduced (the solution turning green)

* Too much stress cannot be laid upon the importance of reducing the ore to the finest possible powder, as the success of the "fusion" hangs entirely upon this point. The ore should be crushed in a steel mortar until the powder is fine enough to pass through a linen bag; it is then ground in an agate mortar with the addition of a little water, until it is reduced to an impalpable powder.—Rideal and Rosenblum (the authors of the method), *Journal of the Society of Chem. Industry*, December 31, 1895.

† Platinum and silver vessels are attacked by the fused peroxide. Nickel is also attacked to some extent, but the dissolved nickel is subsequently removed.

‡ It is essential to the success of the process that the whole of the sodium peroxide be decomposed at this stage, otherwise, when the liquid is subsequently acidified, hydrogen peroxide will be generated, and this, reacting upon the chromate in solution, causes the reduction of a portion of the chromium. The reducing action of hydrogen peroxide upon chromic acid is similar in its character to that which it exerts upon other highly oxidised compounds (*e.g.* peroxides, permanganates, etc.), whereby oxygen is withdrawn from *both* compounds, and is liberated as free gas. In the case of chromium, however, an intermediate stage occurs, in which the blue compound, supposed to be perchromic acid, is first formed.

and the ferrous salt is present in slight excess. That excess of iron has been introduced is ascertained by bringing a drop of the liquid (by means of a glass rod) into contact with a drop of a fresh and *dilute* solution of potassium ferricyanide upon a white plate, when a blue colour is obtained. The stopper is replaced in the weighing-bottle, and the latter set aside to be re-weighed after the titration has been completed.

The excess of ferrous salt present is now determined by means of deci-normal potassium dichromate, which is added until a drop of the liquid no longer gives a blue colour with potassium ferricyanide.

The weighing-bottle is now re-weighed, the difference being the total weight of the ferrous salt used. From this is deducted the weight of ferrous salt equivalent to the volume of deci-normal dichromate employed, *i.e.* the *excess* of ferrous salt, which gives the weight of ferrous salt oxidised by the chromate derived from the ore. From the equation $2CrO_3 + 6FeO = Cr_2O_3 + 3Fe_2O_3$, it will be seen that 1 atom of Cr (52·4) is capable of oxidising 3 atoms of Fe ($56 \times 3 = 168$).

The formula-weight of ferrous ammonium sulphate being exactly seven times the weight of the iron it contains (see p. 334), the weight of this salt which is equivalent to 52·4 parts of chromium is 1176 parts. From this proportion the percentage of chromium in the ore is readily calculated.

Iodine.

Free iodine, in the presence of water and certain oxidisible substances, is able to take the hydrogen from water and liberate the oxygen. The oxygen thus eliminated oxidises the oxidisible compound present, and therefore the iodine acts as an indirect oxidising agent, 127 parts of iodine being equivalent to 8 parts of oxygen.

Thus, when a solution of iodine is added to dilute sulphurous acid, the latter compound is oxidised to sulphuric acid—

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$$

Similarly, the lower oxides of arsenic and of antimony (or the salts of these oxides) are oxidised by iodine in the presence of water; thus with sodium arsenite—

$$Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$$

Therefore a standard solution of iodine may be used to estimate

sulphur dioxide in solution, and also for the determination of arsenic and antimony.

When iodine is added to a *dilute* solution of sulphuretted hydrogen, a definite reaction takes place, which is usually expressed by the equation *—

$$H_2S + I_2 = 2HI + S$$

Hence a solution of iodine may be employed for the direct determination of sulphuretted hydrogen in solution. Of all the reactions for which a solution of iodine is employed, the most useful and important in volumetric analysis is that with thiosulphuric acid, or sodium thiosulphate, which becomes converted into the sodium salt of tetrathionic acid, while hydriodic acid (or the sodium salt) is produced ; thus—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \dagger$$

In volumetric processes in which iodine is employed, the end reaction is indicated by means of starch. When brought in contact with free iodine, starch produces a deep blue coloration, and the formation of this blue colour constitutes a delicate indication of the smallest excess of iodine over and above that which is required for the oxidising reaction in hand.

The blue-coloured substance is usually regarded as a *compound* of starch and iodine, although unstable in character and of unknown composition; the idea of *combination* between the substances is also conveyed by the name *iodide of starch*, by which it is called. Towards sodium thiosulphate, however, in common with many other reagents, it behaves exactly as *free* iodine : if a solution of

* In this equation the *oxidising* character of the process is obscured by the omission from it of the water which is necessary for its progress. At the ordinary temperature, hydrogen sulphide and iodine do not interact in the absence of water. One function of the water is, by dissolving the hydriodic acid, to furnish the necessary heat required for the combination of the hydrogen and iodine; while another, no doubt, is to supply the intermediate step in the process whereby oxygen is available for the oxidation of the sulphuretted hydrogen, thus—

$$I_2 + H_2O + H_2S = 2HI + H_2O + S$$

† This reaction, just as in the case of sulphuretted hydrogen, is in reality one of indirect oxidation through the intervention of water. The mechanism of the reaction will be understood by the following dissected equations—

$$I_2 + H_2O + \begin{matrix} Na \\ Na \end{matrix}\!\!\begin{matrix} NaS_2O_3 \\ NaS_2O_3 \end{matrix} = 2HI + ONa_2 + Na_2S_4O_6$$

$$2HI + ONa_2 = 2NaI + H_2O$$

the thiosulphate be added to it, the iodine at once attacks the thiosulphate according to the above reaction, just as though there were no starch present; and the instant the whole of the iodine is thus used up, the blue colour of the liquid disappears.

It is on this account that a solution of sodium thiosulphate used in conjunction with the iodine solution constitutes so important a volumetric reagent. Thus, all substances which can be made to yield chlorine either directly (as from hypochlorites or chlorates) or indirectly (as by the action of hydrochloric acid upon peroxides, chromates, etc.) are capable of being estimated by these reagents. The liberated chlorine is passed into potassium iodide, and there displaces its equivalent of iodine, and the exact amount of iodine can then be determined by means of sodium thiosulphate.

Deci-normal Iodine Solution.

(12·7 *grams of iodine per litre.*)

12·7 grams of the purest re-sublimed iodine, in a state of powder, are exactly weighed out into a litre flask. About 20 grams of potassium iodide (free from iodate) dissolved in about 200 c.c. of water are added, and the mixture gently shaken until the iodine is wholly dissolved. The solution is then diluted up to the litre with water at 15°, and preserved in a well-fitting stoppered bottle in the dark.

If strictly deci-normal, 1 c.c. will contain 0·0127 grams of iodine, equivalent to 0·0008 gram oxygen or to 0·00355 gram of chlorine.

Deci-normal Sodium Thiosulphate.

(24·8 *grams of* $Na_2S_2O_3,5H_2O$ *per litre.*)

24·8 grams of the purified salt, which has been carefully powdered,* are weighed out into a litre flask, and dissolved in water. The solution is then diluted up to 1000 c.c. with water at 15°. If strictly deci-normal, 1 c.c. of the solution will be exactly oxidised by 1 c.c. of the iodine solution.

Titration of Deci-normal Iodine, by means of sodium thiosulphate.

* When powdering a salt which contains a large number of molecules of water of crystallisation, such as sodium thiosulphate, there is always a risk of a slight loss of water. This is due to the fact that the pressure produced by the blow of the pestle causes the momentary partial liquefaction of portions of the salt. This explains the fact that, although perfectly free from extraneous moisture, such a salt appears to become damp, and "clogs" upon the pestle during the process of powdering. While in this condition the salt may lose traces of its water of crystallisation by evaporation.

Twenty-five cubic centimetres of the deci-normal thiosulphate solution are transferred by means of a pipette to a beaker, diluted with a little water, and a few drops of a clear solution of starch added.* The iodine solution is then run in from a stoppered burette, until a single drop gives a permanent blue coloration.

The titration may equally as well be made in the opposite order. Twenty-five cubic centimetres of the iodine solution are transferred to a beaker, diluted with about an equal volume of water, and the starch solution added. The thiosulphate is then delivered from a burette until the blue colour is just discharged. As a rule, when the titration is made in this way, it is an advantage not to introduce the starch until towards the end of the reaction, especially if the amount of iodine is considerable. The thiosulphate is added until the brown colour of the iodine solution begins to perceptibly pale, and the liquid assumes a straw colour. One or two drops of starch are then introduced, causing the blue colour, and the thiosulphate delivered drop by drop until the colour is discharged.

The result of this titration will show the exact relation in which these two solutions stand to each other. If they bear the correct relative values, then 25 c.c. of the one will require 25 c.c. of the other in order to exactly complete the reaction between them. If, on the other hand, one is found to be proportionately a little stronger than the other, the value of the one in terms of the other must be notified, preferably on the labels of the bottles. Thus, suppose the 25 c.c. of iodine solution required 24·9 c.c. of the thiosulphate solution, then 1 c.c. of the latter equals $\frac{25}{24{\cdot}9}$ or 1·004 c.c. of the iodine; and 1 c.c. of the iodine is equivalent to 0·996 c.c. of thiosulphate.

Although these solutions might be found to bear the exact relative value towards each other, so that equal volumes are chemically equivalent, it is obviously possible that they might still not be strictly deci-normal solutions. It is possible, although perhaps not highly probable, that an error to exactly the same extent might have arisen in the preparation of each; so that each of them

* The starch solution is prepared by mixing about 1 or 2 grams of white potato-starch in powder with 5 or 6 c.c. of cold water in the bottom of a moderately large beaker. A considerable quantity of boiling water is then poured upon it. As the hot water is being added, the opaque white appearance which the mixture presents at first, changes almost suddenly to that of a semi-translucent gelatinous substance. At this point the addition of the boiling water is stopped, and the beaker nearly filled up with cold water. It is allowed to settle, and the clean liquid poured off for use. This starch solution should not be kept for more than one day, or at the outside two days.

should be either too strong or too dilute to the same degree. It is necessary, therefore, to make an independent titration of one of them to serve as a check. Either of the following methods can be used.

(*a*) *Titration of Deci-normal Iodine by means of Arsenious Oxide.*—

$$As_4O_6 + 4I_2 + 4H_2O = 8HI + 2As_2O_5$$

That is to say, 127 parts of iodine will oxidise 49·5 parts of arsenious oxide.

4·95 grams of finely powdered arsenious oxide, which has been purified by resublimation, are exactly weighed out into a litre flask, and about 500 c.c. of water added. Thirty grams of pure sodium bicarbonate are then introduced, and the mixture gently warmed upon a steam-bath to a temperature about 60°, and continually shaken until the arsenious oxide is wholly dissolved.* The solution is then cooled and made up to a litre with water at 15°. This solution, containing one-tenth of the equivalent of arsenious oxide, is of deci-normal strength, 1 c.c. being equivalent to 0·0127 gram of iodine, and therefore equal to 1 c.c. of deci-normal iodine solution.

Twenty-five cubic centimetres of this solution are transferred to a small beaker, a few drops of clear starch solution added, and the deci-normal iodine solution delivered into it from a burette until the blue coloration is permanent. From the volume of the iodine solution required to completely oxidise the arsenious oxide in 25 c.c. of the solution, the exact strength of the iodine solution is obtained. If it is found to be strictly deci-normal, then obviously the thiosulphate solution which has the same relative strength is also exactly deci-normal.

(*b*) *Titration of Deci-normal Thiosulphate Solution by means of Potassium Dichromate.*—When a solution of potassium dichromate,

* An excess of the alkali is necessary in order to neutralise the hydriodic acid which is afterwards produced during the titration, the necessary alkali for this purpose being supplied by sodium bicarbonate, instead of either the normal carbonate or caustic alkali. As already stated, the iodine in this blue compound behaves towards many reagents much as *free* iodine would, and free iodine is dissolved by caustic alkali, and also (but less easily) by the normal carbonates of the alkalies; thus—

$$6NaHO + 3I_2 = 5NaI + NaIO_3 + 3H_2O$$
$$6Na_2CO_3 + 3I_2 + 6H_2O = 6NaHCO_3 + 5NaI + NaIO_3 + 3H_2O$$

Hence if either of these alkaline reagents be added to the blue starch iodide, the blue colour will be destroyed (see note on p. 355).

acidified with hydrochloric acid, is mixed with potassium iodide, and the mixture gently warmed, iodine is liberated ; thus—

$$K_2Cr_2O_7 + 14HCl + 6KI = 3I_2 + Cr_2Cl_6 + 8KCl + 7H_2O$$

The amount of iodine so liberated is the equivalent of the available oxygen in the dichromate, three atoms of available oxygen being equivalent to six atoms of iodine, *i.e.* 8 parts of oxygen liberate 127 parts of iodine.

If a *standard solution* of the dichromate be used in the reaction, the available oxygen is a known quantity, and therefore the amount of iodine it can liberate is also a known quantity ; so that if this iodine be titrated with sodium thiosulphate, the strength of the latter can be determined—

Thus 1 c.c. deci-normal dichromate solution contains 0·0008 gram available oxygen ;
therefore 1 c.c. deci-normal dichromate solution liberates 0·0127 gram iodine.
1 c.c. deci-normal thiosulphate oxidises 0·0127 gram iodine ;
therefore 1 c.c. deci-normal dichromate is equivalent to 1 c.c. deci-normal thiosulphate.

Twenty-five cubic centimetres of deci-normal dichromate solution are placed in a stoppered bottle, and about 2 grams of potassium iodide together with 5 or 6 c.c. of strong hydrochloric acid are added. The mixture is thoroughly shaken, and gently heated by standing the closed bottle in warm water for some time. The bottle with its contents is then cooled, the stopper withdrawn and rinsed into the bottle with water, and the liberated iodine titrated with the thiosulphate solution ; the starch solution being added when the reddish colour of the iodine solution begins to fade. The disappearance of the blue colour of the iodide of starch leaves the solution not colourless, but pale green (due to the chromic chloride), hence a little care is necessary in judging the end reaction.* If the deci-normal thiosulphate is of exact strength, 25 c.c. will be required for the titration.

* Deci-normal permanganate, acidified with dilute sulphuric acid, may be substituted for the dichromate and hydrochloric acid, the operation being conducted in the same manner. In this case, when the blue colour of the starch iodide is discharged by the thiosulphate, the liquid is left colourless. The 5 atoms of available oxygen in permanganate liberate 10 atoms of iodine ; thus—

$$2KMnO_4 + 8H_2SO_4 + 10KI = 5I_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O$$

Estimations by means of Deci-normal Iodine.

(1) Antimony in Antimonious Oxide.

$$Sb_2O_3 + 2H_2O + 2I_2 = 2HI + Sb_2O_5$$

About 1 gram of antimonious oxide is weighed out into a $\frac{1}{4}$-litre flask. Two grams of tartaric acid dissolved in about 25 c.c. of water are then added, and the mixture gently shaken until the antimonious oxide is dissolved. Sodium carbonate (the normal salt) is added until the solution is just neutral, and the liquid is diluted with water to 250 c.c. Fifty cubic centimetres of this solution are withdrawn with a pipette and transferred to a beaker, and from 20 to 30 c.c. of a cold saturated solution of pure sodium bicarbonate * added, together with a few drops of starch. The deci-normal iodine solution is then run in from a burette until a permanent blue colour is produced. A duplicate titration should be made in a second portion of the solution.

EXAMPLE.—Fifty cubic centimetres of the solution required 27·5 c.c. of the iodine solution ;

therefore 250 c.c. (containing 1 gram of the original oxide) would require $27{\cdot}5 \times 5 = 137{\cdot}5$

1 c.c. deci-normal iodine = 0·0127 gram I = 0·0060 gram Sb
= 0·0072 gram Sb_2O_3

therefore $137{\cdot}5 \times 0{\cdot}0060 = 0{\cdot}8250$ gram Sb in 1 gram of the oxide

$\frac{0{\cdot}8250 \times 100}{1} =$ **82·50** percentage Sb, or **99·0** percentage of Sb_2O_3

(2) **Arsenic in Arsenious Compounds.**—The process is carried out as already described on p. 350.

(3) **Tin, in the Condition of Stannous Chloride,** may also be estimated by means of iodine, but in this case the principle involved is different to that which obtains with either arsenic or antimony. Stannous chloride unites directly with iodine, forming the compound $SnCl_2I_2$—

$$SnCl_2 + I_2 = SnCl_2I_2$$

hence two atoms of iodine become the measure of one atom of tin, or 127 parts of iodine are equivalent to 59 parts of tin. Tin cannot, however, be determined by this reaction in the presence of lead ; because, although lead chloride alone is not acted upon by free iodine, it is acted upon by the stannic chlor-iodide with the precipitation of yellow lead iodide, which completely obscures the end reaction. In tin alloys, therefore, which contain lead, the latter metal must be first removed.

* See note on p. 350.

Estimations by means of Iodine and Thiosulphate.

(1) **Sulphur Dioxide in Sodium Sulphite,** $Na_2SO_3,7H_2O$—

$$Na_2SO_3 + I_2 + H_2O = 2HI + Na_2SO_4$$

That is to say, 126 parts of the crystallised salt are oxidised by 127 parts of iodine; therefore 1 c.c. $\frac{N}{10}$ iodine (containing 0·0127 gram I) is equivalent to 0·0126 gram $Na_2SO_3,7H_2O$, or 0·0032 gram SO_2.

About 1 gram of the powdered salt is weighed out into a flask, and 100 c.c. of the iodine solution added. This volume ensures an excess of iodine, so long as the weight of salt taken has not exceeded 1·25 grams,* and the excess will be manifest by the colour of the liquid.

The excess of iodine is now titrated by means of the deci-normal thiosulphate solution, added from a burette. As soon as the brown colour of the iodine begins to pale to a yellow, starch is added, and then the addition of the thiosulphate is continued until the blue colour is discharged. The excess of iodine thus found, deducted from the volume originally taken (100 c.c. in this case), gives the amount of iodine which has been used in oxidising the sodium sulphite in accordance with the above reaction, and from this the percentage of sulphur dioxide can be calculated.†

(2) **Available Chlorine in Bleaching Powder.** — The active ingredient in bleaching powder is the compound expressed by the formula Ca(OCl)Cl. Bleaching powder, however, besides containing some unacted-upon calcium hydroxide, usually contains also more or less chlorinated compounds (such as calcium chlorate, for example), which are of no use for the purposes to which the bleaching powder is put. The chlorine which is present as calcium chloro-hypochlorite, Ca(OCl)Cl, is known as the *available* chlorine. This chlorine is evolved when the bleaching powder is acted upon by dilute acids; thus—

$$Ca(OCl)Cl + H_2SO_4 = H_2O + CaSO_4 + Cl_2$$
$$Ca(OCl)Cl + 2HCl = H_2O + CaCl_2 + Cl_2$$

Hence, if bleaching powder consisted of the pure compound,

* In cases where the composition of the sulphite is unknown, a preliminary titration must be made, using a considerable quantity of iodine, so as to gain an approximate idea of the amount required.

† This method may also be applied for the estimation of sulphuretted hydrogen in solution (as in hepatic waters), and also of aqueous solutions of chlorine and bromine.

having the formula Ca(OCl)Cl, it would contain 55 per cent. of available chlorine ; but in reality this is never the case, and the best samples of commercial bleaching powder seldom exceed about 36 per cent., while in others it falls considerably below this.

About 10 grams of bleaching powder are weighed out into a porcelain mortar, and rubbed down with a small quantity of water until the mixture has the consistency of thin cream. The heavier particles are allowed a moment or two to settle, and the milky liquid is poured off into a litre flask. The residue is then ground down with a little more water, and the process repeated until the last traces have been transferred to the flask. The mixture is then diluted with water up to 1000 c.c., and thoroughly shaken.

Twenty-five cubic centimetres of the milky fluid are transferred by means of a pipette to a small beaker, the contents of the flask being briskly shaken up immediately before the withdrawal of the sample. Excess of potassium iodide is added by introducing 10 c.c. of a solution containing 5 grams KI in 100 c.c. water.* The mixture is then acidified with acetic acid.† This liberates the chlorine from the bleaching powder, and that, in the presence of the excess of potassium iodide, sets free an equivalent quantity of iodine—

$$Cl_2 + 2KI = 2KCl + I_2$$

The amount of the liberated iodine is then estimated by the addition of deci-normal sodium thiosulphate, after the addition of starch.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = 0{\cdot}0127 \text{ gram I} = 0{\cdot}00355 \text{ gram Cl}$$

Therefore the volume of thiosulphate required to discharge the blue colour of the starch iodide, is a measure of the chlorine which was liberated from the bleaching powder contained in 25 c.c. of the original mixture. From this the percentage of available chlorine is calculated.

Valuation of Bleaching Powder. Alternative Method by means of Arsenious Oxide.‡—Instead of estimating the available chlorine

* It is convenient to remember that a suitable excess of potassium iodide will be ensured if twice the weight of potassium iodide is added as there is of bleaching powder present. In the above example, 25 c.c. of the bleach solution contains 0·25 gram of the compound (10 grams to the litre), and the weight of potassium iodide in 10 c.c. of the KI solution is 0·5 gram.

† Acetic acid does not liberate chlorine from any *chlorate* which the bleaching powder may contain.

‡ Although this method does not involve the use of sodium thiosulphate, it is most conveniently introduced at this point.

in bleaching powder by measuring the amount of iodine which that chlorine is capable of liberating, it may be determined by measuring the amount of arsenious oxide which the *oxygen* present in the active constituent of the powder is capable of oxidising. This active ingredient, as stated above, is the calcium chloro-hypochlorite, $Ca(OCl)Cl$, which contains 1 atom of oxygen to every 2 atoms of chlorine. Hence the weight of bleaching powder capable of furnishing 35·5 parts of available chlorine, will also supply 8 parts of oxygen ; this oxygen, therefore, may be taken as the measure of the chlorine—

$$2Ca(OCl)Cl\,^{*} + As_2O_3 = As_2O_5 + 2CaCl_2$$

Twenty-five cubic centimetres of the freshly made and well-shaken up bleaching powder solution are transferred to a small beaker by means of a pipette, and deci-normal arsenious oxide solution † is gradually added from a burette. The end of the reaction

* When bleaching powder is mixed with water, it is converted into calcium chloride and hypochlorite ; thus—

$$2Ca(OCl)Cl = Ca(OCl)_2 + CaCl_2$$

The composition of bleaching powder, therefore, may be, and often is, expressed by the formula $Ca(OCl)_2,CaCl_2$, and it will be obvious that the proportion which the oxygen bears to the chlorine is the same in both cases, *i.e.* 8 parts by weight of O to 35·5 parts of Cl. The compound calcium hypochlorite $Ca(OCl)_2$ itself contains all the oxygen but only half the chlorine originally present in the bleaching powder.

Whether or not the decomposition of the bleaching powder into hypochlorite and chloride by the agency of water is complete, is not known with certainty, probably it is not. Neither is the exact *modus operandi* of the water, in bringing about this decomposition, clearly understood. Probably a cycle of changes takes place, which may be explained by the following equations :—

$$\begin{aligned} Ca(OCl)Cl \\ Ca(OCl)Cl \end{aligned} + H_2O = \underbrace{\begin{matrix} HCl \\ HCl \end{matrix} + Ca\!\!\begin{matrix} OCl \\ OCl \end{matrix}}_{HOCl} + CaO$$

$$= CaCl_2 + \underbrace{\qquad\qquad}_{HOCl} + CaO$$

$$= CaCl_2 + Ca\!\!\begin{matrix} OCl \\ OCl \end{matrix} + H_2O$$

† The deci-normal solution used for estimating the value of bleaching powder must either be *freshly prepared*, as described on p. 350, or else it must be made with *normal sodium carbonate* instead of the bicarbonate, using 20 grams in place of the 30 grams of the latter salt. It has been found in practice that the solution made from the bicarbonate undergoes some change on being kept (the precise nature of which is not known), which introduces errors into the analysis greater than are caused by the action of the normal carbonate upon the starch iodide.

is determined by means of starch and potassium iodide, used as an *outside indicator*. After each addition of the arsenious solution, the mixture is stirred, and a drop of it removed upon a glass rod, and brought into contact with a piece of filter-paper, which has been previously impregnated with a mixture of starch and potassium iodide.* So long as undecomposed bleaching powder is present, the liquid will cause a blue stain upon the paper. The arsenious solution is cautiously added, until a drop of the liquid brought into contact with potassium-iodide-and-starch paper gives no blue colour.

If the exact point is overstepped, a little additional excess of the arsenious solution may be added, together with a few drops of starch, and the excess titrated by means of deci-normal iodine solution, until the blue colour is produced. On deducting this excess from the total volume of the arsenious solution used, the exact volume which was oxidised by the bleaching powder is obtained, and from this the percentage of available chlorine may be calculated.

(3) **Estimation of Manganese Dioxide.**—When manganese dioxide is heated with hydrochloric acid, an amount of chlorine is evolved which is the chemical equivalent of the available oxygen in the manganese dioxide (see p. 337). The chlorine so evolved may be absorbed by means of a solution of potassium iodide, whereby an amount of iodine equivalent to the chlorine (and therefore equivalent to the oxygen) is liberated. The iodine thus set free can then be determined by means of sodium thiosulphate.

About 0·5 gram of the manganese dioxide, in fine powder, is weighed out into a small flask (Fig. 73), about 80 to 100 c.c. capacity. The flask is provided with a delivery tube, which is fitted either by means of a good cork which has been previously soaked in melted paraffin wax, or a rubber stopper which has been boiled in caustic soda in order to remove sulphur; or the tube is made by drawing out a wider tube, the wide portion of which is slightly conical, and has pushed over it a short piece of black rubber tube. This constitutes a perfect fitting stopper and exit tube in one. The delivery tube, bent as shown, passes through a cork into a U-tube placed in a beaker of cold water. The U-tube contains moderately strong potassium iodide solution. (2·5 grams of KI for 0·5 gram

* This paper is readily prepared by adding a small quantity of potassium iodide to a little clear starch solution, and dipping strips of unsized paper into the mixture. If these strips are then hung up to dry, they may be preserved indefinitely in a stoppered bottle.

of MnO_2 will ensure a suitable excess.*) A few fragments of magnesite are introduced into the flask along with the manganese ore, and about 25 to 30 c.c. of strong hydrochloric acid added. The delivery tube is then attached, and a gentle heat applied to the flask. The object of the magnesium carbonate is to furnish a slow stream of carbon dioxide during the entire operation (magnesite being only slowly dissolved by the acid), which not only sweeps out the chlorine, but prevents the liquid in the absorption tube from being sucked back into the flask during the last stages of the

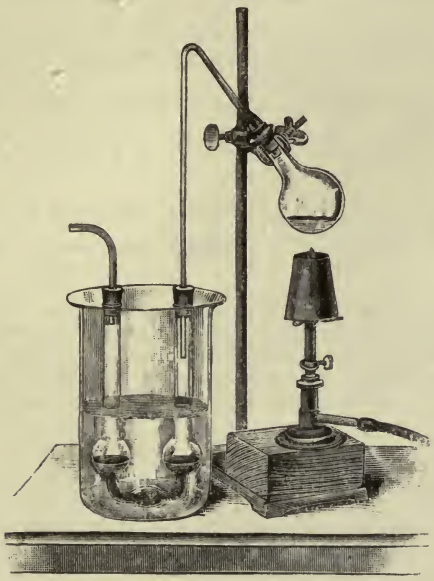

FIG. 73.

operation when the acid is being boiled. As the chlorine enters the potassium iodide solution it is wholly absorbed, so long as the evolution of the gas is not allowed to proceed too fast. When the manganese dioxide has all passed into solution, the temperature is raised to the boiling-point, and the liquid allowed to boil for a few minutes. When the distillation is completed, the U-tube is disconnected, and the contents washed out and diluted to 100 c.c. in

* A second U-tube is sometimes connected to the first to serve as a guard, lest any chlorine should escape unabsorbed from the first. This, however, will not happen unless the distillation is made far too rapidly.

a graduated flask. Twenty-five cubic centimetres of this solution are withdrawn by means of a pipette, and the liberated iodine is then estimated by titration with deci-normal sodium thiosulphate. As soon as the brown colour of the liquid fades to yellow, a little starch is added, and the addition of the thiosulphate continued until the blue colour is just discharged.

EXAMPLE.—Weight of manganese dioxide taken = 0·495 gram. Iodine solution diluted to 100 c.c.; 25 c.c. of the liquid

required of $\frac{N}{10}$ thiosulphate (1 c.c. = 0·0127 gram I) ... 21 c.c.

$0{\cdot}0127 \times 21 = 0{\cdot}2667$ gram iodine in 25 c.c.

and $0{\cdot}2667 \times 5 = 1{\cdot}3335$ gram iodine liberated by 0·495 gram of the ore

From the equation $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2 (= I_2)$,

127 parts of iodine are liberated by 43·5 parts of manganese dioxide—

Therefore 127 : 1·3335 :: 43·5 : 0·45674 = grams of MnO_2

and $\frac{0{\cdot}45674 \times 100}{0{\cdot}495} = \mathbf{92{\cdot}27}$ = percentage of MnO_2 in the ore

A number of other oxygenated compounds are susceptible of being estimated by the same method, namely, by distillation with hydrochloric acid, and causing the evolved chlorine to liberate its equivalent of iodine. Thus, a chromate treated in this manner yields 3 atoms of chlorine for each (CrO_3) group according to the equations—

$$K_2CrO_4 + 8HCl = 4H_2O + 2KCl + (CrCl_3) + 3Cl$$
$$K_2Cr_2O_7 + 14HCl = 7H_2O + 2KCl + 2(CrCl_3) + 6Cl$$

Similarly, a chlorate, when treated with hydrochloric acid, yields a mixture of chlorine and chlorine peroxide, which is capable of liberating iodine to the extent of 6 atoms of iodine for each (ClO_3) group; thus—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + \underbrace{9Cl + 3ClO_2}$$
$$9Cl + 3ClO_2 + 24KI = 12KCl + 6K_2O + 24I$$

Or the relation of the chlorate to the available oxygen may be more clearly seen by the following equations :—

$$(1) \qquad KClO_3 = KCl + 3O$$
$$(2) \quad 3O + 6HCl = 3H_2O + 6Cl$$

In the case of bromates and iodates, only 4 atoms of chlorine are disengaged for each group (BrO_3) and (IO_3), and therefore only

4 atoms of iodine are liberated when the evolved gas is passed into potassium iodide. The reason for this difference is due to the fact that one-third of the chlorine is taken up in decomposing the molecule of potassium bromide (or iodide), forming potassium chloride and the monochloride of the halogen, which remain behind in the distilling-flask; thus—

$$(1) \quad KIO_3 = KI + 3O$$
$$(2) \quad 3O + 6HCl = 6Cl + 3H_2O$$
$$(3) \quad KI + 6Cl = KCl + ICl + 4Cl$$

SECTION IV.

Volumetric Methods based upon Precipitation.

The number of volumetric processes which fall into this section is extremely large. In the following typical examples some depend upon precipitation alone, while others are based upon precipitation in conjunction with one of the other methods described in the foregoing sections.

I. Precipitation by means of Silver Nitrate.

Deci-normal Silver Nitrate Solution.

(16·966 *grams of* $AgNO_3$ *per litre.*)

4·2415 grams* of pure silver nitrate are exactly weighed out into a 250-c.c. flask, and dissolved in water. The solution is made up to the quarter litre with cold water.

One cubic centimetre of this solution contains 0·010766 gram Ag, and is equivalent to 0·00355 gram Cl.

(1) **Estimation of Chlorine in Sodium Chloride.**—About 1 gram of pure sodium chloride is weighed out and dissolved in water, the solution being diluted up to 250 c.c.

Fifty cubic centimetres of this solution are transferred to a beaker by means of a pipette, and three or four drops of a solution of potassium chromate† added to serve as indicator. The deci-normal silver solution is then gradually run in from a burette.

As soon as the whole of the chlorine is precipitated, in the form of silver chloride, any additional silver nitrate interacts with the chromate, precipitating red silver chromate. As soon, therefore, as a drop of the silver nitrate produces a permanent reddish tinge in the liquid, the titration is complete.

* Unless a number of determinations are to be made, it is not necessary to prepare more than a quarter of a litre of the silver solution.

† The neutral or yellow chromate K_2CrO_4. For this titration the solutions must be neutral and cold

The process may be once or twice repeated for the sake of practice; and in order to gain experience in detecting the first appearance of the red colour, a second beaker, containing about an equal volume of sodium chloride and the chromate indicator, to which a few drops of silver nitrate solution have been added, may be placed alongside the one in which the titration is being made, so as to compare the colours.*

Alternative Method.—The precipitation of chlorine by silver nitrate (or *vice versâ*, of silver by means of a soluble chloride) is one of the very few examples of a precipitation process in which the end reaction can be determined without recourse to a third substance as indicator. This is due to the peculiarities of the precipitate, which allow of its ready subsidence, leaving a clear liquid after being shaken. Moreover, the chromate indicator is inadmissible in the presence of acids (silver chromate being soluble); hence, before it can be employed, the solution to be titrated, if acid, must be first carefully neutralised with sodium carbonate. The following method is carried out in an acid solution :—

Fifty cubic centimetres of the solution of sodium chloride prepared as above, are transferred to a well-fitted stoppered bottle (narrow mouth), and a few drops of strong nitric acid added. The bottle should be screened from bright daylight during the process. This is conveniently done by rolling a strip of black paper (or common brown paper) into a short cylinder about the same height as the bottle, and into which the bottle will just fit; or the bottle may be wrapped in a black cloth. The deci-normal silver is then added from a burette, a considerable proportion of the total quantity required being run in at once. The bottle is then briskly shaken without exposure to daylight, and the precipitate allowed to settle. If any floats or adheres to the sides, it can be made to sink by gently tapping the bottle upon the table. As soon as the liquid has clarified, more of the silver is added, and the shaking repeated. This is repeated until the addition of the silver solution causes no further precipitation. As the point is reached when the precipitation is nearly complete, the solution clarifies less readily; hence, until experience is gained, the exact point of completion is liable to be overstepped. It is desirable, therefore, when the precipitation

* Instead of the chromate indicator being employed, the chlorine may be completely precipitated by the addition of an excess of the deci-normal silver, a few drops of nitric acid being first added. The mixture is then filtered, and the excess of silver present in the solution is determined by titration with ammonium thiocyanate, with a ferric salt as indicator (see p. 365). Bromides and iodides may be determined in the same manner.

is judged to be complete, to add a few drops of deci-normal sodium chloride from a burette (see p. 364), which, if excess of silver has been added, will cause a further turbidity in the liquid. The amount of silver equivalent to the deci-normal sodium chloride thus added, is deducted from that which has been used.

In cases where the chloride is present only in very small quantities, as in the estimation of chlorides in natural waters, the analysis may be carried out by the first of the methods here given. If the second process be employed, a carefully measured volume (about 20 c.c.) of deci-normal sodium chloride should be added to 50 c.c. of the water, and the mixture titrated with the deci-normal silver. The volume of the silver solution equivalent to the amount of *added* chlorine, deducted from the total silver solution used, gives the amount of silver required to precipitate the chlorine originally present in the water.

(2) **Estimation of Cyanogen in Potassium Cyanide.**—When excess of silver nitrate is added to potassium cyanide, the reaction which takes place is analogous to that between silver nitrate and potassium chloride, silver cyanide being precipitated—

$$KCN + AgNO_3 = AgCN + KNO_3$$

And therefore 1 c.c. $\frac{N}{10}$ silver nitrate, containing 0·01766 gram Ag, is equivalent to 0·0026 gram (CN). Silver cyanide, however, is soluble in potassium cyanide, molecule for molecule, forming the double cyanide (soluble) KCN,AgCN ; therefore, when silver nitrate is gradually added to a solution of potassium cyanide, the first action is the formation of this double salt ; thus—

$$2KCN + AgNO_3 = KCN,AgCN + KNO_3$$

As soon as the whole of the potassium cyanide has been converted into this soluble double salt, the addition of more silver results in its decomposition and the precipitation of silver cyanide ; thus—

$$KCN,AgCN + AgNO_3 = 2AgCN + KNO_3$$

Hence the completion of the first stage can be taken as the end reaction, which will be indicated by the first appearance of a permanent precipitate.

For the completion of the first stage, 1 c.c. $\frac{N}{10}$ silver nitrate will be equivalent to $0{\cdot}0026 \times 2 = 0{\cdot}0052$ gram (CN) or 0·0130 gram KCN.

The first step in the reaction between silver nitrate and potassium cyanide is not interfered with by the presence of soluble

halides (chlorides, bromides, iodides). If, therefore, a chloride be added to the solution, no silver chloride is formed until the cyanide has been entirely converted into the double salt. When that stage is complete, then the further addition of silver nitrate results in the precipitation of silver chloride. In fact, the completion of the first reaction is more distinctly seen by introducing a few drops of sodium chloride solution to serve as indicator, than by depending on the decomposition of the double cyanide and the precipitation of silver cyanide.

About 0·5 gram of potassium cyanide is weighed out and dissolved in water in a 100-c.c. flask, and the liquid diluted up to the graduation. Twenty-five cubic centimetres of this are transferred to a small beaker by means of a pipette, and deci-normal silver nitrate added from a burette until the first indications of a faint permanent precipitate appear. The beaker should be placed upon a dead black surface. A second portion may be similarly titrated after the addition of one or two drops of a dilute solution of sodium chloride to serve as the indicator.

(3) **Indirect Estimation of Nitric Acid in Nitre.***—If potassium nitrate is evaporated with strong hydrochloric acid, the radical (NO_3) is exchanged for (Cl); that is to say, nitric acid is expelled, and potassium chloride is left—

$$KNO_3 + HCl = KCl + HNO_3$$

The residue, after being heated for a short time to about 120°, is dissolved in water, the solution diluted to a definite volume, and aliquot portions titrated with deci-normal silver, using the chromate indicator. The *chlorine* which is estimated is thus the measure of the nitric acid, 35·5 parts of Cl displacing 62 parts of (NO_3) or 54 parts of (N_2O_5). Therefore 1 c.c. $\frac{N}{10}$ silver is equivalent to 0·0062 gram (NO_3) or 0·0054 gram (N_2O_5).

The nitrate of any metal which is thus capable of being converted into a chloride, and whose chloride can be heated without undergoing decomposition or volatilisation, may be determined in this way.

(4) **Indirect Estimation of Calcium in Calcium Carbonate.**—The calcium carbonate is dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue is dissolved in water and again evaporated to dryness, and finally heated to about 120° to expel the excess of acid. The residue consisting of calcium chloride is dissolved in water, diluted to a definite volume, and the chlorine estimated in an aliquot portion by means of silver. The

* The four following examples serve to indicate the various ways in which indirect estimations can be made by means of standard silver nitrate.

chlorine is thus the measure of the calcium, 35·5 parts of chlorine being equivalent to 20 parts of calcium—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

Hence 1 c.c. $\frac{N}{10}$ silver is equivalent to 0·0020 gram of Ca.

(5) **Indirect Estimation of Carbon Dioxide in Sodium Carbonate.**—The sodium carbonate is dissolved in water, and precipitated with barium chloride. The barium carbonate is filtered and thoroughly washed, and then dissolved upon the filter in dilute hydrochloric acid. The liquid is thoroughly washed through the filter and evaporated to dryness at least twice (as directed above), and afterwards heated to about 120°. It is then dissolved in water, and made up to a definite volume. An aliquot portion is taken and a slight excess of sodium sulphate added, in order to precipitate the barium. The chromate indicator is then added (the precipitate of barium sulphate exerting no disturbing influence upon the titration), and deci-normal silver run in until the red colour appears—

$$Na_2CO_3 + BaCl_2 = 2NaCl + BaCO_3$$
$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$$

The chlorine estimated is the measure of the carbon dioxide, 2 atoms of Cl being equivalent to 1 molecule of CO_2; or 35·5 parts of Cl are equivalent to 22 parts of CO_2. Hence 1 c.c. $\frac{N}{10}$ silver is equivalent to 0·0022 gram of CO_2.

(6) **Indirect Estimation of Cadmium in Cadmium Sulphate.**—The sulphate is converted into carbonate by precipitation with sodium carbonate. The precipitate is filtered, washed, and dissolved in hydrochloric acid. The solution is evaporated to dryness once or twice, and the residue heated to expel the excess of acid. It is then dissolved, and the chlorine in it estimated by deci-normal silver with chromate indicator—

$$CdSO_4 + Na_2CO_3 = CdCO_3 + Na_2SO_4$$
$$CdCO_3 + 2HCl = CdCl_2 + CO_2 + H_2O$$

Chlorine is thus the measure of cadmium, 35·5 parts of Cl being equivalent to 56 parts of cadmium. Therefore 1 c.c. $\frac{N}{10}$ silver is equivalent to 0·0056 gram Cd.

II. Precipitation by means of Sodium Chloride.

Deci-normal Sodium Chloride Solution.

(5·85 *grams* NaCl *per litre.*)

5·85 grams of purified sodium chloride are weighed out and dissolved in water, the solution then being diluted up to 1 litre.

One cubic centimetre contains 0·00585 gram NaCl, or 0·00355 gram Cl, and is equivalent to 0·010766 gram Ag.

Estimation of Silver.—The details of the process are practically the same as for the estimation of chlorine by means of silver, p. 360. When the chromate indicator is used to determine the end reaction, it should not be added to the silver nitrate; but a measured volume of the sodium chloride should be delivered into a beaker, the indicator added to this, and the silver solution delivered from a burette until the red colour makes its appearance.

III. Precipitation by means of Ammonium Thiocyanate.

Deci-normal Ammonium Thiocyanate Solution.

(7·6 *grams of* $(NH_4)CNS$ *per litre.*)

About 8 grams of the crystallised salt (which is too deliquescent to allow of exact weighing) are roughly weighed out and dissolved in a litre of water. The solution is then titrated by means of deci-normal silver nitrate.

When ammonium thiocyanate is added to silver nitrate, a white precipitate is produced, consisting of silver thiocyanate, insoluble in nitric acid—

$$AgNO_3 + (NH_4)CNS = AgCNS + NH_4NO_3$$

This reaction takes place even in the presence of a ferric salt, and it is not until the whole of the silver has been precipitated that the characteristic blood-red ferric thiocyanate makes its appearance. A ferric salt, therefore (but obviously not the *chloride*), constitutes an extremely delicate indicator for this reaction. The most convenient ferric salt is the sulphate, a solution of which may be prepared by dissolving a few crystals of ferrous sulphate in water in a boiling-tube, adding about half the volume of strong nitric acid (pure), in order to oxidise the iron, and then briskly boiling the mixture for a few minutes, to expel all the nitrous fumes. This solution, which is acid with excess of nitric acid, is then somewhat diluted with water, and a measured volume—say 3 or 4 c.c.—should be uniformly employed in the titrations.*

Titration of the Thiocyanate Solution.—Twenty-five cubic centimetres of deci-normal silver nitrate are transferred to a small flask, and 4 c.c. of the ferric sulphate solution added.† The

* When a number of titrations are to be made, the ferric solution should be made up of some definite strength, and the same volume of it used for each operation.

† The presence of nitric acid is necessary, and if the ferric sulphate solution is prepared as described, it will contain sufficient acid.

solution of the ammonium thiocyanate is then run in from a burette. As each drop enters the mixture, the red colour of ferric thiocyanate appears for a moment, but at once disappears on gently shaking the flask. The solution is cautiously added until the first indications of a permanent red coloration are seen. From the volume used, the exact strength of the thiocyanate solution is ascertained, and the amount of dilution which it requires in order to bring it strictly to deci-normal strength is readily calculated. After the solution has been thus adjusted, it should be once more titrated.

1 c. c. $\frac{N}{10}$ thiocyanate contains 0·0076 gram $(NH_4)CNS$, and is equivalent to 0·010766 gram Ag, 0·00355 gram Cl, or 0·0127 gram I.

(1) **Estimation of Silver.**—The estimation of silver is conducted exactly as in the titration of the standard thiocyanate solution. The presence of other metals, as lead, copper, zinc, exerts no disturbing effect so long as the solution contains free nitric acid. Hence the silver in such an alloy as silver coinage, may be determined directly in the nitric acid solution, by diluting the liquid to a definite volume, and titrating an aliquot portion with deci-normal thiocyanate, and the ferric sulphate indicator.

(2) **Indirect Estimation of Chlorine (Bromine or Iodine).**—The solution of the chloride is acidified with nitric acid, and precipitated by the addition of a measured excess of deci-normal silver nitrate. The mixture is briskly shaken and filtered, and the precipitate washed free from silver nitrate. The filtrate and washings are then titrated with deci-normal thiocyanate, after the addition of the ferric indicator. The excess of silver nitrate thus ascertained, deducted from the total volume taken, gives the amount which was used in precipitating the chlorine; and from this the percentage of the halogen is calculated.

The necessity for filtering the solution lies in the fact that silver chloride is dissolved by alkaline thiocyanate. Silver bromide is less easily affected, while upon silver iodide it exerts practically no solvent action.

IV. Precipitation by means of Uranium Acetate.

When a solution of uranium acetate or nitrate* is added to a solution of an orthophosphate, in the presence of sodium acetate

* These compounds are often spoken of as *uranyl* salts, and are represented as containing the divalent group $(UO_2)''$, analogous to the monovalent groups, bismuthyl, BiO (in basic bismuth nitrate, or *bismuthyl* nitrate, $(BiO)NO_3,H_2O$), and antimonyl, SbO (in tartar emetic, $(SbO)K(C_4H_4O_6)$).

and acetic acid, a yellow precipitate of uranium phosphate is produced, according to the equation—

$$(UO_2)''(C_2H_3O_2)_2 + HNa_2PO_4 = 2Na(C_2H_3O_2) + H(UO_2)''PO_4$$

The completion of the reaction may be determined by means of a solution of potassium ferrocyanide, used as an *outside* indicator. As soon as the uranium solution is in excess, the ferrocyanide gives a red-brown coloration with a drop of the mixture brought in contact with it upon a white plate.

Standard Uranium Acetate, $(UO_2)''(C_2H_3O_2),2H_2O$.—This solution is made of such a strength that 1 c.c. is equivalent to 0·005 gram P_2O_5.

From the equation given above, it will be seen that 425·8 parts of the crystallised salt are equivalent to $\frac{142}{2} = 71$ parts of P_2O_5; hence—

71 : 5 :: 425·8 : 29·986 = weight of uranium acetate required per litre *

About 31 or 32 grams, therefore, of the crystallised salt are weighed out and dissolved in water in a litre flask, with the addition of 30 to 40 c.c. of glacial acetic acid. The solution is then diluted up to 1000 c.c. with water.

Titration of the Uranium Solution. (*a*) *By means of Hydrogen Disodium Phosphate.*—10·085 grams of pure recrystallised hydrogen disodium phosphate (which has not become effloresced by exposure to the air) are exactly weighed out and dissolved in water, the solution then being made up to one litre.

One cubic centimetre of this solution will contain 0·002 gram, P_2O_5. It is therefore two-fifths of the strength of the standard uranium solution, 20 c.c. of which should be equivalent to 50 c.c. of the sodium phosphate.

Fifty cubic centimetres of the sodium phosphate solution (containing 0·1 gram, P_2O_5) are transferred to a beaker by means of a pipette, and heated until it *just begins* to boil † (the titration is best made at a temperature about 95°). The uranium solution is then run in from a burette, until, on placing a drop of the hot

* If uranium nitrate, $(UO_2)''(NO_3)_2,6H_2O$, be used instead of the acetate, the exact weight of the salt per litre to give a solution of the same value will be 35·47 grams, the formula-weight of this salt being 503·8. About 36 or 37 grams, therefore, should be weighed out.

† If uranium nitrate has been employed, 5 c.c. of a 10-per-cent. solution of sodium acetate must be added. This is not necessary in the case of uranium acetate, as by double decomposition alkaline acetate is produced during the titration.

mixture upon a plate, and adding a drop of potassium ferrocyanide to it, a red-brown coloration is seen.*

Duplicate titrations giving concordant results having been made, the exact value of the uranium solution is ascertained, and if necessary, it may be diluted by the addition of the requisite amount of water to bring it to the correct strength. Thus if 19 c.c. instead of 20 c.c. were required for the titration of 50 c.c. of the phosphate, then every 190 c.c. must be made up to 200, and the solution titrated once more. If the solution is more nearly exact, say 19·5 c.c. being required instead of 20 c.c., it may be employed in this state, and the volume used in an analysis must then be multiplied by the necessary factor ; in this case $\frac{20}{19{\cdot}5} = 1{\cdot}02564$.

(*b*) *By means of Tricalcium Phosphate.*—In order to accurately determine phosphoric acid in its combinations with lime or magnesia (as in bone-ash, for example), it is necessary that the uranium solution should be titrated upon a solution of calcium phosphate, so that the conditions of the titration of the standard solution may be the same as those obtaining in the actual analysis.

The solution of tricalcium phosphate, $Ca_3(PO_4)_2$, employed is prepared so as to contain 5 grams of the phosphate per litre. This corresponds very nearly to the strength of the sodium phosphate solution above, and contains 0·00229 gram P_2O_5, per cubic centimetre.

A quantity of the purest commercial tricalcium phosphate is weighed out, which contains exactly 5 grams of $Ca_3(PO_4)_2$.† This

* The formation of the red-brown coloration (uranium ferrocyanide) is influenced by the presence of varying quantities of other salts (alkaline acetates, etc.), which may be present. It is therefore necessary to make the conditions *as nearly as possible the same in all cases.* The same volumes of solutions of approximately the same strength and at the same temperature being used; and the same interval of time allowed for the development of the brown colour with the indicator. Again, if the uranium solution is to be employed for estimating phosphoric acid in solutions which contain ammonia (such as in urine, for example), a definite quantity of ammonium acetate (5 c.c. of a 10-per-cent. solution to 50 c.c. of the liquid) should be added to the solution of sodium phosphate when standardising the uranium solution.

† Even the purest commercial product cannot be trusted to consist wholly of tricalcium phosphate, therefore it is necessary to estimate the phosphoric acid in the particular sample used, by gravimetric methods. For this purpose a weighed quantity, about 0·4 to 0·6 gram, is dissolved in nitric acid, and completely precipitated by means of ammonium molybdate. After standing in a warm place some hours (conveniently all night), the precipitate is washed first by decantation, and finally upon a filter with water containing ammonium molybdate and nitric acid. It is then dissolved in ammonia, and the phosphoric acid precipitated as ammonium magnesium phosphate by the addition of "magnesia mixture," and finally weighed as magnesium pyrophosphate (see p. 264). From the phosphoric acid thus found the percentage of $Ca_3(PO_4)_2$ in the commercial calcium phosphate is calculated.

is dissolved in the smallest quantity of hydrochloric acid, and the solution diluted to 1000 c.c.

Fifty cubic centimetres of this solution are then transferred to a beaker, 5 c.c. of a 10-per-cent. solution of sodium acetate, together with 3 or 4 drops of acetic acid, are added, and the uranium solution run in from a burette until nearly the whole amount necessary has been added.* The mixture is then heated to about 95°,† and the titration continued by adding the uranium solution cautiously, until a drop of the solution withdrawn on a rod and tested with potassium ferrocyanide gives the first indications of red-brown coloration.

Estimation of Phosphoric Acid in Bone-ash.—About 1·5 grams of bone-ash, which has been dried in a steam-oven, are weighed out and dissolved in the least possible quantity of strong hydrochloric acid. The solution is then diluted to 250 c.c. with water. Fifty cubic centimetres of this solution are transferred to a beaker, and 5 c.c. of sodium acetate (10-per-cent. solution) added, together with 3 or 4 drops of acetic acid.

Uranium acetate (standardised by means of calcium phosphate) is then added from a burette, until the first indications of colour are perceived when a drop of the mixture is tested on a white plate with a drop of potassium ferrocyanide. The solution is then heated to 90°–95°, and again tested. If the coloration again appears, the titration is complete; if not, the uranium solution is added drop by drop, until the liquid gives a faint colour with the indicator. A second titration is then made, in which nearly the whole volume of uranium (which the first experiment has shown to be required) is added at once before the mixture is heated, and the process finally completed in the hot solution.

V. Precipitation by means of Sodium Sulphide.

When a solution of sodium sulphide is added to an ammoniacal solution of a zinc salt, zinc sulphide is precipitated, the end of the

* When *standardising* the uranium solution, the volume required to be added is known beforehand within a very near limit; but when estimating phosphoric acid in a phosphate of unknown composition, the first titration will be made with a view to ascertain approximately the volume of uranium required, after which a second experiment is made more exactly.

† It is necessary that the solution should not be heated until nearly the whole of the phosphoric acid has been precipitated by the uranium solution, otherwise the calcium phosphate itself will be precipitated, and will then no longer interact with the uranium. This difficulty is sometimes evaded by conducting the titration in the reverse way, *i.e.* by heating a measured volume of the uranium solution in a beaker, and adding the solution of the phosphate from a burette until a drop of the liquid just ceases to give a coloration with ferrocyanide.

reaction being indicated by means of either an alkaline lead solution or sodium nitroprusside, used as *outside* indicators.

Standard Sodium Sulphide Solution.—A solution of convenient strength should contain about 12 grams of Na_2S per litre, and may be prepared as follows: 12 grams * of sodium hydroxide are weighed out, and dissolved in 50 c.c. of water. One-half of this solution is then saturated with sulphuretted hydrogen, after which the other half is added, and the mixture thoroughly shaken. If the solution still smells of the gas, a small additional quantity of sodium hydroxide is added, and the liquid diluted to one litre.

Titration of the Sodium Sulphide Solution.—The solution of the sodium sulphide is titrated by means of a standard solution of zinc sulphate, which is made of such a strength that 1 cc. shall contain 0·01 gram Zn. Such a solution is prepared by weighing out 44·15 grams of pure crystallised zinc sulphate, $ZnSO_4,7H_2O$, dissolving in water, and diluting up to 1 litre.†

Twenty-five cubic centimetres of this solution are transferred to a beaker by means of a pipette, a small quantity of ammonium carbonate added, and then ammonia, until the precipitate is entirely redissolved. The sodium sulphide solution is gradually delivered into this mixture from a burette, with constant stirring. The progress of the operation is watched by withdrawing a drop of the liquid upon the end of a fine glass rod, and bringing it into contact with a drop of sodium nitroprusside upon a white plate. As soon as the slightest excess of sodium sulphide is present, a violet colour is imparted to the nitroprusside solution. The alkaline lead solution, which may be used as indicator in place of the nitroprusside, is made by adding a solution of lead acetate to a mixture of tartaric acid with an excess of caustic soda, and heating the solution until it is clear. Drops of this solution are placed at intervals upon a piece of filter-paper, and a drop of the solution undergoing titration is placed near to, but not immediately upon, one of these.‡ As the latter drop spreads and touches the lead

* The formula-weight of Na_2S and 2NaHO being almost identical, namely, 78 and 80.

† This solution is a little over three times the strength of a deci-normal solution, which would contain 14·35 grams of the salt per litre. An alternative method of preparing the solution is to dissolve 10 grams of pure zinc in the smallest excess of dilute sulphuric acid, and then make the solution up to 1 litre with water.

‡ The reason for not bringing the drop immediately upon the indicator is, that any of the precipitate of ZnS which is brought out upon the drop of the mixture would be decomposed by the lead salt, with formation of lead sulphide,

solution, a black or brown stain of lead sulphide will be shown as soon as the sodium sulphide is in excess. If the sodium sulphide solution contains exactly 12 grams of Na_2S per litre; then 1 c.c. (containing 0·012 gram Na_2S) will be equivalent to 0·04415 gram of $ZnSO_4,7H_2O$, or to 0·01 gram of Zn, as deduced from the following equation :—

$$ZnSO_4,7H_2O + Na_2S = ZnS + Na_2SO_4 + 7H_2O$$
$$287 \qquad 78$$
$$287 : 78 :: 0{\cdot}04415 : 0{\cdot}012$$
$$\text{or } 65 : 78 :: 0{\cdot}01 : 0{\cdot}012$$

Hence 25 c.c. of the zinc solution would be exactly precipitated by 25 c.c. of the sodium sulphide.

Estimation of Zinc in Zinc Ores or Alloys. — In the analysis of zinc-blende (p. 279) or of bronze (p. 274), the zinc may be estimated by the volumetric process here given. The solution is rendered alkaline by the addition of excess of a mixture of ammonium carbonate and ammonia, and the standard sodium sulphide added from a burette, until a drop of the liquid withdrawn upon a glass rod produces a brown coloration with the alkaline lead indicator when applied in the manner described above.

As the sodium sulphide solution rapidly undergoes change, it should be titrated against the standard zinc solution shortly before being used.

Other metals, *e.g.* cadmium and copper, may also be estimated by means of sodium sulphide.

VI. Clark's Method for estimating the Hardness of Water.*—This is a process of precipitation by means of a standard solution of soap. The soap (potassium oleate) interacts with the calcium and magnesium salts present in the water, with the precipitation of calcium and magnesium oleates. In this process, the soap solution itself serves as the indicator, not by any colour-change, but by its property of causing a *lather* to form when water containing the solution is shaken up. So long as the hardness-producing salts are undecomposed by the soap, no lather is formed on shaking the mixture, but directly the soap solution is in excess a permanent lather is instantly raised on shaking. By this method of estimating hardness, the *total* hardness is first determined. Another portion is then boiled until the temporary hardness is destroyed by the

and the titration would appear to be complete when in reality it was not. By depositing the drop at some little distance from the area wetted with the lead solution, the zinc sulphide precipitate is retained where the drop first touches, and only the *solution* is able to extend, by capillarity, along the paper.

* For Hehner's acidimetric method, see p. 328.

decomposition of the soluble bicarbonates, and the *permanent* hardness estimated in the sample. The difference between the two estimations represents the *temporary* hardness.

Standard Potassium Oleate Solution.—A strong solution of this soap is first prepared by rubbing together in a mortar 75 grams of the so-called "lead plaster" of the druggist (*plumbi emplast.*, Brit. Pharm., which consists practically of lead oleate) and 20 grams of dry potassium carbonate. When the two are thoroughly incorporated, a small quantity of methylated alcohol is added, and the mixture worked up into the consistency of a thin smooth cream. More spirit is then added, and the contents of the mortar rinsed, by means of spirit, into a bottle, and the mixture placed aside to settle. The clear liquid is decanted off through a filter, and the sediment finally washed upon the filter with more spirit. The volume of the liquid may now be made up to 200 or 250 c.c. by adding a mixture of equal volumes of spirit and water.

Titration and Adjustment of the Soap Solution.—For this purpose a standard solution of calcium chloride is prepared, containing 0·222 gram of $CaCl_2$ per litre. This is equivalent to 0·200 gram $CaCO_3$ per litre, and 50 c.c. will therefore be equivalent to 0·01 gram of $CaCO_3$.

0·2 gram of pure *calcite*, or *iceland spar*, is exactly weighed out and dissolved in dilute hydrochloric acid in a covered vessel, preferably a platinum dish. The solution is then evaporated to dryness upon a steam-bath. The residue is treated with water, and the solution again taken down to dryness. This process should be once or twice repeated in order to ensure the removal of all the acid. The residue is finally dissolved, and the solution made up to 1 litre.

Fifty cubic centimetres are then transferred to a stoppered bottle of about 250 c.c. capacity by means of a pipette.* The soap solution is then added from a burette 1 *c.c. at a time*, and the contents of the bottle briskly shaken after each addition. As the point is approached when a lather is raised, the volume added each time is reduced, and the process continued until the lather remains permanent for two minutes, the bottle being laid upon its side.

From this preliminary experiment, the amount of dilution which the soap solution will require, in order that exactly 14·25 c.c. shall be necessary to produce the permanent lather with 50 c.c. of the

* The contents of the pipette must be allowed to flow out *without being blown out by the breath* (see p. 307), because it is very important to avoid introducing any carbon dioxide into the bottle, as this gas affects the soap solution.

calcium chloride solution, can be calculated. The soap should then be diluted by the addition of a mixture of methylated spirit and water in equal volumes, so as to reduce its strength *nearly, but not quite, to this strength*—say to such a strength that about 13·5 c.c. shall give the lather with 50 c.c. of the standard calcium chloride.

It is then allowed to stand in a stoppered bottle for 24 hours, during which time a slight sediment usually settles out, and the solution slightly loses strength. It is then decanted or filtered, and titrated again against 50 c.c. of the lime solution, and finally adjusted to the exact strength by the addition of more alcohol and water.

14·25 c.c. of the soap will therefore be equivalent to 0·01 gram $CaCO_3$; and 0·01 gram $CaCO_3$ in 50 c.c. of water equal 20·00 parts in 100,000, or 20 degrees of hardness.

(1) **Estimation of the Total Hardness in Ordinary Tap-water.**—Fifty cubic centimetres of the water are introduced into the stoppered bottle as above (see footnote), and briskly shaken in order to expel dissolved carbon dioxide, and the air in the bottle is then either swept out by means of a current of air from a pair of bellows (the blowpipe bellows), or is sucked out by means of a glass tube. The soap solution is then added, 1 c.c. at a time at first, but diminishing to one or two drops as the operation proceeds, with a brisk shake up after each addition. As soon as the soap is in excess and a permanent lather will remain for two minutes, the bottle being placed upon its side, the titration is complete, and the degree of hardness corresponding to the volume of soap solution employed is ascertained from the *table of hardness* (see Appendix). If the sample of water is so hard that 50 c.c. require more than 16 c.c. of the soap, the water must be diluted by taking, say, half this volume, and diluting it up to 50 c.c. with distilled water which has been recently boiled for 10 minutes to expel carbon dioxide, and quickly cooled. The degree of hardness which this diluted sample contains is doubled in order to express the actual hardness of the water.

(2) **Estimation of the Permanent Hardness in Water.**—One hundred and fifty cubic centimetres of the water are placed in a half-litre flask and counterpoised upon a rough balance. The water is gently boiled for half an hour in order to completely precipitate the salts which cause the *temporary* hardness. It is then cooled and replaced upon the balance, and cold, recently boiled distilled water added until the original weight is restored. The water is then filtered (the filter being used without being previously

wetted), and 50 c.c. of the clear filtrate titrated with the standard soap solution, as in the previous case.

The difference between the permanent and total hardness gives the temporary hardness.

Appendix to Section IV.

Estimation of Copper by means of Potassium Cyanide.—When a solution of potassium cyanide is added to an alkaline solution of a copper salt, a soluble double cyanide is formed (see p. 87). As this compound is colourless, while the original copper solution is blue, the end of the reaction is readily seen by the disappearance of the blue colour.

Standard Potassium Cyanide Solution.—This solution is made of such a strength that 1 c.c. shall be equivalent to 0·005 gram of copper. As the solution cannot be made of the exact strength by weighing out the actual quantity of cyanide required, an approximate solution is first prepared by dissolving about 25 grams of potassium cyanide in a litre of water. The precise copper-value of this solution is then determined by titration against a standard copper solution, from which the exact amount of dilution necessary to reduce it to the required strength is calculated.

Titration and Adjustment of the Cyanide Solution, by means of Standard Copper Solution.—Five grams of pure electrolytic copper are weighed out into a litre flask, and dissolved in a mixture consisting of equal volumes of strong nitric acid and water. The flask may be gently warmed upon a steam-bath. When this metal is wholly dissolved, the solution is cooled and diluted up to 1 litre with cold water.

One cubic centimetre of this solution will contain 0·005 gram Cu.

Twenty-five cubic centimetres of the standard copper solution are transferred to a beaker, and made alkaline by the addition of a slight excess of sodium carbonate (the solution of sodium carbonate being cautiously added, and the beaker covered, to avoid loss from effervescence).

To this mixture, in which the precipitate is suspended, is added, by means of a pipette, 1 c.c. of ammonia solution, prepared by mixing 1 volume of strong ammonia (sp. gr. 0·88) with 2 volumes of water. This dissolves the precipitate, and produces a deep blue solution.* The potassium cyanide solution is then delivered into

* The reason for neutralising with sodium carbonate before adding ammonia, is to avoid the introduction of ammoniacal salts, which by their presence

this solution from a burette, until the blue colour is just discharged. The amount of dilution which the cyanide solution requires in order to reduce its strength to the exact standard, *i.e.* so that 25 c.c. of the copper solution shall require exactly 25 c.c. of the cyanide, is calculated, and the necessary water added.

Thus, suppose 21 c.c., instead of 25, were required in the first titration, then 210 c.c. must be diluted to 250 c.c., or 840 c.c. will be diluted to 1 litre.

Estimation of Copper in Copper Ores.*

Epitome of Process.—The ore is dissolved in hydrochloric and nitric acids, and after filtration and dilution, the copper is precipitated by means of a rod of metallic zinc in contact with a piece of platinum. The spongy copper is washed, and then dissolved in nitric acid. The solution is made alkaline with sodium carbonate, the precipitate dissolved by the addition of ammonia, and the blue liquid is finally titrated with standard potassium cyanide in the cold.

Exactly 5 grams of the ore, in fine powder, are weighed into a flask, and gently warmed with a mixture of 40 c.c. of strong hydrochloric acid and 10 c.c. of water. Six cubic centimetres of a mixture of strong nitric acid and water in equal volumes are then added, and the solution kept gently simmering for about half an hour, after which it is briskly boiled for about 10 minutes.

The insoluble gangue is then separated by filtration, the filter being thoroughly washed, and the copper precipitated from the warm liquid by introducing into it a rod of zinc, upon which a strip of platinum is loosely twisted. It is essential that there shall be an excess of zinc, the rod therefore should weigh about 50 grams, and should be as free from lead as possible. In about half an hour the whole of the copper will be precipitated, after which the zinc rod is withdrawn (leaving the platinum in the vessel, as a portion of the copper is deposited upon it), and rinsed into the beaker. The spongy copper is washed free from zinc chloride and other dissolved salts by carefully decanting the liquid, and once or twice washing the precipitate by decantation. The last wash-water is drained

influence the decolorising of the copper solution by the cyanide. This is sometimes obviated to a considerable extent by evaporating the acid solution of the copper down to dryness, to expel the acid. In the ordinary process of the analysis of copper ores, however, this involves much loss of time, hence the acid solutions are neutralised as here described, and therefore the standardisation of the potassium cyanide solution should be conducted with a copper solution under similar conditions as obtain in the analyses for which the cyanide is employed.

* The method here given for the estimation of copper is essentially that known as the "Mansfield," or as Steinbeck's (the discoverer) process.

away as thoroughly as possible, and the spongy copper (both that which is loose, as well as that which is deposited on the platinum) is dissolved by adding 16 c.c. of nitric acid (1 volume strong acid to 1 volume water). The solution is then diluted to 100 c.c. with water.*

Fifty cubic centimetres of this solution are transferred to a beaker, made alkaline by the addition of sodium carbonate, 1 c.c. of ammonia (1 volume strong ammonia to 2 volumes of water) added, and the blue solution titrated with the standard cyanide. The number of cubic centimetres of the cyanide used, multiplied by 2, gives the volume which would be required for the whole of the copper solution ; and since each cubic centimetre of the cyanide is equivalent to 0·005 gram Cu, and since, also, 5 grams of the ore were employed for analysis, the number of cubic centimetres of cyanide, multiplied by 0·1, gives at once the percentage of copper in the ore. For example, suppose the 50 c.c. of the copper solution required 41 c.c. cyanide, then—

$41 \times 2 = 82$ cc. = cyanide required for the *whole* of the copper in the 5 grams of ore

1 c.c. cyanide = 0·005 gram Cu

therefore $82 \times 0{\cdot}005 = 0{\cdot}410$ gram Cu in 5 grams ore

and $\frac{0{\cdot}410 \times 100}{5} = \mathbf{8{\cdot}2}$ per cent. of copper

or $82 \times 0{\cdot}1 = \mathbf{8{\cdot}2}$

* If the ore contains less than 6 per cent. of copper, the reduced metal may be dissolved in half this volume of nitric acid, the solution diluted somewhat, and whole solution used for one titration.

SECTION V.

Gas Analysis.

General Principles.—The principles upon which the various methods of gas analysis are based are themselves extremely simple, although in some cases the apparatus employed, and the manipulative details involved, are often somewhat complicated and intricate.

This is more especially the case when the analysis is to be carried out with that high degree of refinement and exactness which is often necessary in scientific research. Until comparatively recent times these exact, extremely slow, and somewhat recondite methods of gas analysis were practically the only processes available; but of late years the demand for simpler and more rapid methods, sufficiently exact for technical purposes, has resulted in the invention of numerous forms of "gas apparatus" which are capable of yielding good results with the minimum expenditure of time and trouble.*

The methods by which gases are estimated may be classified in the following order:—

(1) **By Absorption in a Suitable Reagent, and Subsequent Titration.**—For example, the carbon dioxide present in a gaseous mixture, such as the atmosphere, may be estimated by bringing a known volume of the gas into contact with an excess of a standard solution of barium hydroxide. Barium carbonate is thereby precipitated, and the excess of barium hydroxide is determined by titration with standard oxalic acid.

Or, again, the chlorine present in the exit gases from the "bleach" chambers may be estimated by aspirating a measured volume of the gas through a solution of potassium iodide, and subsequently determining the liberated iodine by titration with sodium thiosulphate.

(2) **By Absorption, and Subsequent Measurement of**

* For a description of the more refined and elaborate methods of gas analysis, the student is referred to Sutton's "Volumetric Analysis." In this book only the simpler processes will be described.

the Residual Gas.—For example, the carbon dioxide in a mixture of gases is determined by exposing a measured volume of the mixture to the action of caustic potash, and after the whole of the carbon dioxide has been absorbed, the volume of the residual gas is measured. The difference, or the *contraction*, represents the carbon dioxide which was present.

(3) **By the Combustion of the Gas, with the Subsequent Measurement of the Contraction, and Estimation of the Carbon Dioxide, if any is formed.**—For example, hydrogen in a gaseous mixture may be estimated by adding to a known volume of the gas a measured volume of oxygen (or air) more than sufficient to combine with all the hydrogen. These are caused to unite (by methods described later), and the "contraction" ascertained by again measuring the gas. Since 2 volumes of hydrogen and 1 volume of oxygen unite to form water (which then practically occupies no volume), two-thirds of the contraction represents the hydrogen originally present.

When the gas to be estimated contains carbon and hydrogen (as in marsh gas, ethylene, etc.), after the contraction due to combustion has been measured, the volume of carbon dioxide produced is determined by absorption with caustic potash and measurement of the residue, as in (2) above.

I. Estimation of Gases by Absorption and Subsequent Titration.

(*a*) **Carbon Dioxide in the Air** (Pettenkofer's method).

Epitome of Process.—The sample of air to be examined is contained in a large glass jar of known capacity, which can be closed with a well-fitting bung. The temperature of the gas and the atmospheric pressure are noted. A measured volume of a solution of barium hydroxide of known strength is introduced into the jar, and thoroughly shaken up with the enclosed air until the carbon dioxide is entirely absorbed. Aliquot portions of the solution are then withdrawn, and titrated with a standard solution of oxalic acid.

Standard Oxalic Acid.—In order to simplify the subsequent calculations, the strength of the oxalic acid solution may be arranged so that 1 c.c. is equivalent to 1 c.c. of carbon dioxide measured under standard conditions—that is to say, 1 c.c. of the acid is capable of saturating a quantity of barium hydroxide which would be decomposed by this volume of carbon dioxide, the weight of which is 0·00197 gram.

Oxalic acid solution of this strength would contain 5·6442 grams of the crystallised acid, $H_2C_2O_4,2H_2O$, in one litre; but since dilute solutions of oxalic acid are unstable, it is better to prepare the solution of ten times this strength, and dilute it when required.

56·442 grams, therefore, of the pure dry crystallised compound are exactly weighed out, dissolved in cold air-free water,* and the solution made up to one litre. For use, 10 c.c. are transferred to a 100-c.c. flask by means of a pipette, and the solution diluted up to 100 c.c. with air-free water.

Barium Hydroxide Solution (*baryta-water*).—Forty to fifty grams of crystallised barium hydroxide, $Ba(HO)_2,8H_2O$, are roughly powdered, and placed in a large stoppered bottle, and a litre of water added. The mixture is thoroughly shaken from time to time until the water is saturated, after which it is allowed to settle. The clear liquid is decanted off or filtered into a stoppered bottle, and diluted with an equal volume of air-free water.† The stopper of the bottle should be greased with resin cerate, so as to exclude the air as much as possible.

A large glass bottle or jar‡ (whose mouth is sufficiently wide to admit the hand and arm, so that it may be readily wiped dry with a glass-cloth) is fitted with a good bung, preferably of rubber. A hole is bored in the bung, and this hole is closed with a small cork (see Fig. 74). The capacity of the jar is ascertained by filling it with water up to the bung, and then measuring the volume of the water. The capacity, which should not be *less* than 6 litres, and may with advantage be 8 or 10 litres, should be scratched upon the vessel.

The jar is filled with the air to be tested, by leading into it, right to the bottom, a piece of rubber tube, which is attached to a pair of bellows (either hand or foot-bellows), and blowing a stream of air for several minutes in order to ensure the complete displacement

* Distilled water which has been recently boiled to expel carbon dioxide, and quickly cooled.

† This solution will roughly approximate the same relative strength as the oxalic acid above mentioned. A solution of *exactly* equivalent strength, of which 1 c.c. = 0·00197 gram CO_2 (*i.e.* 1 c.c. CO_2 at N.T.P.), would contain 14·11 grams of $Ba(HO)_2,8H_2O$ per litre. Such a solution cannot be obtained by direct weighing, as, the salt being efflorescent, its state of hydration is uncertain; and it also absorbs atmospheric carbon dioxide. A saturated solution at the ordinary temperature contains about 32 grams per litre; hence if this be diluted with its own volume of water, the solution, as first prepared, will contain about 16 grams per litre. As the solution constantly undergoes change by the absorption of atmospheric carbon dioxide, its value must be determined every time it is used, by titration against the standard oxalic acid.

‡ The glass jars used by confectioners answer the purpose very well.

of the air already in the vessel. The bung is then inserted. The temperature of the air in the immediate vicinity of the bottle is noted, and also the height of the barometer at the time.

One hundred cubic centimetres of the baryta-water are then delivered into the jar by means of a pipette, through the hole in the bung, and the cork quickly replaced. The liquid is then made to wet the interior surface of the glass by slowly revolving the vessel upon its side; and it is left in contact with the gas, being shaken up at intervals, for about half to three-quarters of an hour, by which time the whole of the carbon dioxide will be absorbed.

While this absorption is going on, the exact value of the baryta-water is determined by transferring 25 c.c. to a small beaker, and adding the dilute standard oxalic acid from a burette until the liquid ceases to give any indication of a brown colour when a drop of it is placed upon a piece of turmeric paper by means of a glass rod. As the alkali is gradually neutralised by the oxalic acid, the brown colour, which at first is very evident, gradually shows more and more as a faint fringe of colour round the edge of the moistened spot upon the turmeric paper, until finally it disappears.

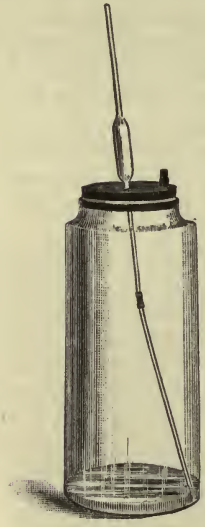

FIG. 74.

Suppose, for example, that 27·5 c.c. of the oxalic acid are used, then 100 c.c. of this baryta solution would require 110·0 c.c. of the oxalic acid to exactly neutralise it.

When the absorption of the carbon dioxide is complete, 25 c.c. of the turbid liquid are withdrawn by means of a pipette, to which a piece of narrow glass tube has been attached in order that it may reach to the bottom of the jar. This is introduced through the hole in the bung, in the manner shown in the figure, and when the pipette is full, the piece of tube is detached, and the liquid allowed to drip from the pipette until it reaches the graduation mark. The measured volume is then transferred to a beaker, and titrated with the oxalic acid as quickly as possible, so as to expose it to the air for the shortest time. The end of the reaction is indicated by means of turmeric paper used as described above.*

* The oxalic acid has no action upon the precipitated barium carbonate. Some chemists use a *dilute* standard hydrochloric acid instead of oxalic acid; either a $\frac{N}{100}$ solution, or one arranged so that 1 c.c. is equivalent to 0·001 gram

A duplicate titration should be made with a second portion of the liquid.

Since 25 c.c. (out of the 100 c.c. of baryta-water originally placed in the jar) have been used for the titration, the volume of oxalic acid used, multiplied by four, will give the amount of oxalic acid required to neutralise the 100 c.c. of baryta-water after the absorption of the carbon dioxide in the known volume of air. This obviously will be less than that required by 100 c.c. of the original baryta-water by just the volume of carbon dioxide which was contained in the sample of air.

EXAMPLE.—

Capacity of glass jar = 10·5 litres
temperature of sample = 16°
barometer reading = 767 mm.

then $\frac{10{\cdot}5 \times 273 \times 767}{289 \times 760}$ = **10·01** litres = volume of the sample reduced to N.T.P.

Value of the baryta solution—

100 c.c. = 110 c.c. of the standard oxalic acid

100 c.c. of the baryta used for absorption ; 25 c.c. taken out for titration.

25 c.c. required 26·45 c.c. standard oxalic acid
∴ 100 c.c. would require 26·45 × 4 = 105·80 c.c. oxalic acid.
110 − 105·80 = 4·2 c.c. = the volume of oxalic acid which is equivalent to the carbon dioxide absorbed by the 100 c.c. of baryta-water

But since 1 c.c. oxalic acid = 1 c.c. CO_2 at N.T.P.
4·2 c.c. „ = 4·2 c.c. CO_2 present in 10·01 litres (or 10,010 c.c.) of air

therefore $\frac{4{\cdot}2 \times 100}{10{,}010}$ = **0·0419** = percentage of CO_2 by volume

(*b*) Estimation of Sulphur Dioxide in Furnace Gases.

Epitome of Process.—By means of a pipe inserted into the flue, a measured volume of the furnace gases is aspirated, with a suitable aspirator, through a known volume of a dilute standard solution of iodine. The excess of iodine is then titrated with a standard solution of sodium thiosulphate.

The **standard solutions** used for this estimation may be the $\frac{N}{10}$ solutions described on p. 348, in which case 1 c.c. of the iodine

CO_2. Hydrochloric acid of such a strength that 1 c.c. shall be equivalent to 0·00197 gram CO_2 (*i.e.* 1 c.c. CO_2) cannot be used, as this would act upon the precipitated barium carbonate.

(and therefore indirectly 1 c.c. of the thiosulphate) is equivalent to 0·0032 gram of sulphur dioxide. It is more convenient, however, and simplifies the calculations, to employ solutions of such a strength that 1 c.c. shall equal 1 c.c. SO_2 measured at N.T.P., *i.e.* 0·002867 gram SO_2 instead of 0·0032 gram.

Such solutions will contain 11·379 grams of iodine, and 22·22 grams of sodium thiosulphate per litre respectively, and they may be prepared either by weighing out these quantities, or by diluting the ordinary $\frac{N}{10}$ solutions; 100 c.c. of the $\frac{N}{10}$ solution (both the iodine and the thiosulphate) being diluted to 111·6 c.c.*

In cases where the percentage of sulphur dioxide in the gas under examination is very small, it is better to employ solutions of one-tenth this strength, in which 1 c.c. is equivalent to 0·1 c.c. SO_2.

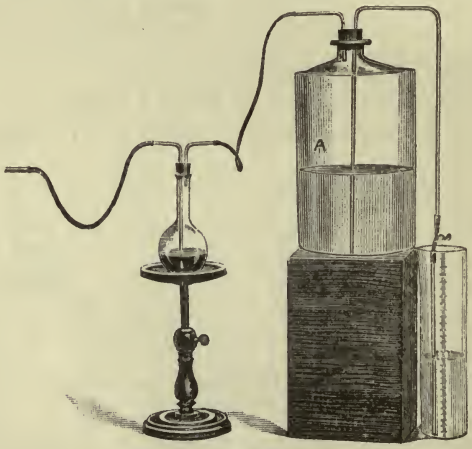

Fig. 75.

One hundred cubic centimetres of the standard iodine solution are placed in a flask fitted with a cork carrying two tubes, one reaching to the bottom, while the other ends just below the cork, as shown in Fig. 75. The former of these tubes is connected to a piece of narrow metal pipe, which is thrust into the flue through

* Standard solutions of such a strength that 1 c.c. = 1 c.c. of the gas to be estimated (at N.P.T.) are sometimes spoken of as *normal solutions*, or *normal gas solutions*. The use of the term *normal solution* for any other solution than those already described on p. 313, is greatly to be deprecated, as tending to introduce confusion.

which the furnace gases are passing.* The other tube is attached to the large bottle A, filled with water, which serves as an aspirator. The water is allowed to flow slowly out of the bottle by means of the screw clamp, and is received in a litre cylinder. The flask containing the iodine is shaken at frequent intervals during the process.

When the cylinder is full to the litre mark, it is either changed, or the clamp is closed for a moment while the cylinder is emptied, and then reopened; a record being made of the number of litres thus drawn off.

During the experiment the temperature of the water is taken (which will be the temperature of the gas), and the height of the barometer is noted.

When 8 or 10 litres† of gas have in this way been aspirated through the iodine solution, the process is stopped, and 25 c.c. of the iodine are transferred to a beaker and titrated with the standard thiosulphate. As soon as the red-brown colour of the iodine solution changes to a straw colour, one or two drops of dilute starch solution are added, and the thiosulphate admitted drop by drop, until the blue colour is discharged. A duplicate titration is made in a second portion of the solution.

EXAMPLE.—Gas drawn from the flue of a coke furnace.‡

Volume of water drawn from aspirator	8 litres
Temperature	17°
Atmospheric pressure	760 mm.

$$\text{Therefore volume of gas operated upon} = \frac{8 \times 273}{290} = 7{\cdot}5307 \text{ litres at N.T.P.}$$

* This pipe should be bent at a right angle at a short distance from the end, and a number of small holes bored along the bent part, while the extreme end is closed either with a metal plug or by being roughly hammered together. In this way the gas is drawn from various points in the horizontal sectional area of the flue.

† When the gas is very rich in sulphur dioxide, as, for instance, in the flue gases from the sulphur-burners in vitriol works, a much smaller volume, say 1 litre, need only be drawn through the apparatus. In such a case, the pipes leading from the absorption flask to the flue must be filled with the flue gases before the tube is attached to the flask. Also, in the final correction of the volume of gas operated upon, the volume of sulphur dioxide which has been absorbed must be added to the volume of water measured out of the aspirator. In the example here given, where the amount of sulphur dioxide is small, these corrections would not affect the third decimal figure.

‡ The furnace had been running many hours previous to taking this sample, and at the time the analysis was made, the draught of air was checked by partially closing the inlet at the bottom. These conditions were arranged in order to intentionally send up the percentage of sulphur dioxide somewhat.

100 c.c. of iodine employed in the absorption flask

(1 c.c. = 1 c.c. thiosulphate = 0·1 c.c. SO_2 at N.T.P.)

After absorption, 25 c.c. iodine solution required 17 c.c. thiosulphate.

$\therefore$ volume of thiosulphate required for 100 c.c. = $17 \times 4 = 68$ c.c.

and volume of SO_2 absorbed = $\frac{100-68}{10} = 3{\cdot}2$ c.c.

Hence 7530·7 c.c. of the furnace gases contain 3·2 c.c. SO_2

or $\frac{3{\cdot}2 \times 100}{7530{\cdot}7} = \mathbf{0{\cdot}425}$ percentage SO_2 by volume

II. Estimation by Absorption, and Measurement of the Residual Gas.

These processes differ from the foregoing, in that they involve (1) the manipulation of comparatively small volumes of gas, and (2) the accurate measurement of these volumes.

For the manipulation of small volumes of gas special apparatus is required, and for the accurate measurement of gaseous volumes special precautions are necessary.

The Measurement of Gases.—The gas whose volume is to be measured must be contained in a graduated and accurately calibrated tube,* and confined over a suitable liquid. Since no gas is *absolutely* insoluble in water, the confining liquid which is used in the most exact processes of gas analysis is mercury; but, in the simpler forms of apparatus about to be described, the confining liquid is water, which, with certain precautions, and in the case of a considerable number of gases, can be employed with fairly accurate results.

The apparatus in which the measurements are made is shown in Fig. 76. This is known as a gas-burette, and consists of a graduated measuring-tube, M, and a pressure-tube, P. The measuring-tube has an ordinary stop-cock at the top, and is furnished at the bottom with a three-way tap, which allows of communication being established with the pressure-tube or with the outer air at will. This will be seen more clearly in Fig. 77. The space between the two taps has a capacity of 100 c.c., and is graduated into cubic centimetres, with subdivisions of fifths of a

* Formerly these tubes were called "eudiometers," from the Greek, signifying *to measure the clearness or goodness of air;* and this term is still usually applied to such vessels when mercury is employed to confine the gas. It has become the custom, however, in the more modern forms of gas apparatus to call these measuring-tubes "gas-burettes."

cubic centimetre,* and the graduations are numbered in both directions. Each of the tubes is fitted into a loaded wooden foot or stand, cut in the manner shown in the figure, so that the tubes may be brought as near together as possible when adjusting the level of the liquid to the same height in each. The foot of the

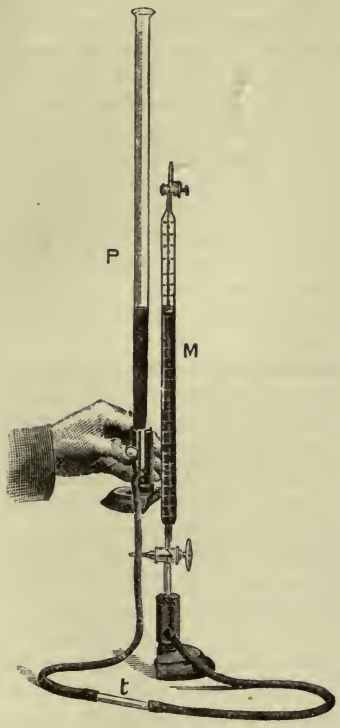

FIG. 76.

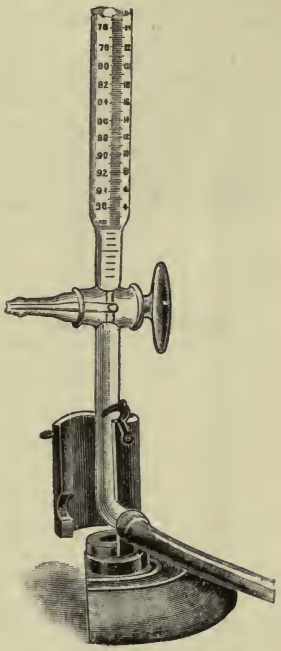

FIG. 77.

measuring-tube is made in the form of a clamp, which is shown open in Fig. 77.

The two tubes are connected by means of a rubber tube, long enough to allow one of the tubes to be raised to the top of the

* The apparatus here figured is Hempel's modified Winkler's gas-burette. In the simple "Hempel" burette there are no taps at all, the top being closed with a piece of rubber tube and a pinch-cock.

other. In order to avoid taking this rubber tube off and on the burette when the latter requires cleaning, it is better to introduce a piece of glass tube as a connector, as shown at *t*. When the measuring-tube and pressure-tube have to be disunited, the separation is made by removing this glass connector.

The gas in the measuring-tube is confined over water, and its volume is measured at atmospheric pressure, which is secured by placing the pressure-tube in such a position relative to the measuring-tube that the water stands at the same level in each (Fig. 76). When reading the volume of the gas, the lower line of meniscus is taken, just as when reading the volume of liquid in an ordinary burette, and the aids may be employed to render the meniscus visible, as are described on p. 310. Before reading the volume of a gas, a *regular* interval of time should be allowed for the water to drain down the walls of the burette; 60 seconds is a suitable time.

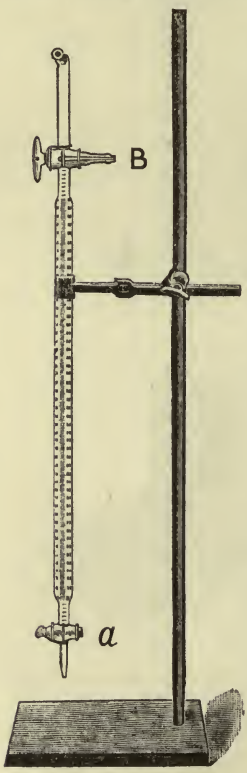

FIG. 78.

Calibration of the Gas-burette.—Just as in the case of the ordinary burette used for liquids, the gas-burette requires to be calibrated before being used for analytical purposes. This is done in the following way. The measuring-tube is disconnected from the pressure-tube at the glass union *t* (Fig. 76), and (without its foot) is supported in an inverted position in an ordinary clamp, as shown in Fig. 78. The tap *a* is opened, and B is turned so as to communicate between the burette and the rubber tube. A beaker of water, at the temperature of the room, is brought under the bottom end of the pipette, and the liquid sucked up until the burette is filled above the tap B, when the *bottom* tap is closed, and the rubber removed. By cautiously opening *a* (B being left open all the time), water is allowed to drop out until the liquid is just level with the under side of the tap B, when *a* is again closed.

A definite volume (3, 4, or 5 c.c.) of the water is then run out

at a time,* and weighed exactly in the manner described on p. 309; and from the weight so obtained, the true capacity of the graduations upon the tube are calculated and tabulated, as in the case of ordinary burettes for liquids.

Correction of Gaseous Volumes.—The volume which a given weight of gas will occupy depends upon three conditions, namely (1) the *temperature*, (2) the *pressure*, and (3) the *degree of humidity* of the gas, at the time the measurement is made.

In order, therefore, that the various volumes observed during an analysis shall be comparable with each other, it is necessary either that the conditions mentioned should remain constant throughout, or that the volumes measured under different, but observed, conditions, should be reduced by calculation to a common standard.

In exact methods of analysis, the latter plan is invariably adopted; but in the more rapid and somewhat rougher methods employed for technical purposes, the analysis may usually be carried out without disturbing the uniformity of the conditions to an extent which will introduce any material error in the results.

The recognised standard to which gaseous volumes are reduced, is the volume which the gas would occupy at 0° and under a pressure of 760 mm., when in the dry state.

(*a*) *Temperature Correction.*—The coefficient of expansion of gases is taken as 0·003665, or $\frac{1}{273}$; therefore the volume at 0° equals the volume at $t°$ divided by $1 + 0{\cdot}003665t$;

$$\text{hence } V_0 = \frac{V}{1 + 0{\cdot}003665t} \quad \text{or} \quad \frac{V \times 273}{273 + t}$$

where V_0 = volume at 0°, and V = volume at $t°$.

(*b*) *Pressure Correction.*—The volume of a gas being inversely as the pressure—

$$V_0 = \frac{VP}{760}$$

where V = the volume at P pressure: or, making both corrections together—

$$V_0 = \frac{VP}{760(1 + 0{\cdot}003665t)} \quad \text{or} \quad \frac{VP \times 273}{760 \times (273 + t)}$$

(*c*) *Aqueous Vapour.*—The aqueous vapour present in a gas exerts a pressure in opposition to the barometric pressure; hence the volume of a gas is increased by the presence of aqueous vapour.

* At the narrow part of the burette, near the tap *a*, each graduation should be calibrated.

If the gas is *saturated* with aqueous vapour, and an excess of water, however minute, be present, then the pressure or *tension* of the aqueous vapour is independent of change of *pressure*, varying only with change of temperature. The *tension of aqueous vapour* has been exactly determined for every degree of temperature within limits, and in the table in the Appendix will be found the tension or pressure, in millimetres of mercury, of the vapour of water between the temperatures of 5° and 25°.

In making the necessary correction for aqueous vapour, therefore, the number of millimetres of mercury representing the tension of aqueous vapour at the particular temperature at which the gas measurement is made, is deducted from the barometric pressure to which the gas is exposed. For example, suppose a volume of gas is measured at atmospheric pressure when the barometer is at 760 mm., and the temperature is 15°; then, on referring to the table, the tension of aqueous vapour at 15° is seen to be 12·7 mm. Deducting this from the barometric pressure gives 760 − 12·7 = 747·3 mm. as the true pressure.

If p stands for the pressure due to aqueous vapour, then the formula—

$$V_0 = \frac{V(P - p)}{760(1 + 0{\cdot}003665t)} \quad \text{or} \quad \frac{V(P - p) \times 273}{760 \times (273 + t)}$$

embraces all the corrections necessary to reduce a volume of a gas, saturated with aqueous vapour, to the standard conditions.

When gases are confined over water, as in the Hempel-Winkler burette, the condition of complete saturation with aqueous vapour is of course always present.* With this apparatus also, the gas-volumes are always read at the atmospheric pressure; and as the analytical operations are rapidly performed, changes of barometric pressure sufficient to influence the results need not be anticipated.

Changes of temperature, however, must be guarded against as far as possible, and with this object in view, the apparatus should be handled entirely by the wooden feet, and not by the glass portions. In order to ascertain the temperature of the gas and see how far it is being maintained uniform throughout, a simple and convenient plan is to suspend a thermometer inside the pressure-tube P (Fig. 76) by means of a thread, so that it reaches nearly to the bottom, and remains there during the whole analysis. As the water is continually being passed backwards and forwards from

* When mercury is employed as the confining liquid, complete saturation of the gas with aqueous vapour is ensured by introducing a drop of water into the measuring-tube, or eudiometer.

the pressure-tube to the measuring-tube, the temperature of the gas may be taken as the same as that of the water over which it is confined; and if the temperature of the latter does not materially change, that of the gas may be considered as practically uniform.

As stated above, when the conditions under which gas measurements are made are constant, it is not necessary to reduce the observed volumes to standard conditions. This will be rendered more obvious by the following concrete example.*

The original volume of gaseous mixture in the burette measured 100 c.c. at atmospheric pressure (*i.e.* when the water was at the same level in both tubes, M, P (Fig. 76). One constituent, x, was then removed by absorption, and the gas measured again. Its volume now was 75 c.c. at atmospheric pressure.

The temperature was 15°, and the barometric pressure 755 mm. throughout.

Then (1) without making reduction to standard conditions, we get—

$$100 - 75 = \mathbf{25} = \text{percentage of } x \text{ in the mixture}$$

(2) On reducing the two volumes by means of the formula $V_0 = \frac{V(P - p)}{760(1 + 0{\cdot}003665t)}$, we get—

$$(a)\ V_0 = \frac{100 \times (755 - 12{\cdot}7)}{760 \times (1{\cdot}055)} = 92{\cdot}56$$

$$(b)\ V_0 = \frac{75 \times (755 - 12{\cdot}7)}{760 \times (1{\cdot}055)} = 69{\cdot}43$$

therefore $92{\cdot}56 - 69{\cdot}43 = 23{\cdot}13 =$ volume of x in 92·56 c.c. original gas

and $\frac{23{\cdot}13 \times 100}{92{\cdot}56} = \mathbf{25} =$ percentage of x in the mixture.

Since the tension of aqueous vapour is independent of *pressure*, then, in the event of any alteration of the barometric pressure taking place during an analysis, it is only necessary to make a correction for pressure; not necessarily by reducing *all* the volumes to the standard, but by reducing all to the same pressure as any one of them.

Thus, in the above example, suppose that between the two measurements the barometer fell from 755 to 750 mm., the temperature remaining constant at 15°, then the following are the data:—

Original volume = 100 c.c. at 15° and 755 mm.
After absorbing x, volume = 75 „ 15° „ 750 „

* The student who has not had practice in the reduction of gases to normal conditions, is strongly recommended to carefully work out these calculations for himself.

then $\frac{75 \times 750}{755} = 74{\cdot}5$ = volume which the residual gas would occupy if measured under the same conditions as the original volume

hence $100 - 74{\cdot}5 = \mathbf{25{\cdot}5}$ = percentage of x in this mixture

If now, from the above data, the two volumes be reduced to standard conditions by means of the formula, as in the last example, it will be found that the same result is obtained, namely, 25·5 percentage of x.

Again, since the tension of aqueous vapour depends upon the temperature, increasing with rise of temperature, change of temperature obviously will produce an alteration of the pressure, even though the *barometric* pressure remains constant. For example, suppose in the above illustration the 100 c.c. original volume is measured at 15°, and the 75 c.c. residual gas is measured at 20°, the barometer standing uniformly at 760 mm.; then the *actual* pressure in the first case is 760 − 12·7 (tension of aqueous vapour at 15°), and in the second it is 760 − 17·4 (the tension at 20°).

Hence, if any change of temperature is observed in the gas during the progress of an analysis, the observed volumes must be reduced to the standard by means of the formula $V_0 = \frac{V(P - p)}{760(1 + 0{\cdot}003665t)}$.*

Collection of Gas for Analysis.—If the gas for analysis is collected in the laboratory, say, a sample of ordinary coal-gas, it may be introduced into the burette by first placing the measuring-tube on a higher level than the pressure-tube, and allowing the former to empty. By means of the three-way tap, communication between the measuring-tube and the outer air is then opened, and a rapid stream of the gas passed through the tube from the top,

* In the Appendix there will be found a table of factors for reducing volumes of gas to standard temperature and pressure, by the use of which much time and calculation will be saved. In the columns opposite to the pressure and temperature at which a gas has been measured, a figure is found, which when multiplied into the observed volume will at once give the corrected volume. Thus, suppose 60 c.c. of gas saturated with aqueous vapour were measured at 12° with the barometer standing at 766 mm. Then—

$766 - 10{\cdot}5$ (tension aq. vap. at 12°) $= 755{\cdot}5$ mm. = actual pressure

On referring to the table, the figure in the 12° column which falls halfway between 755 and 756 mm. is 0·9522;

therefore $60 \times 0{\cdot}9522 = 57{\cdot}132$ = corrected volume

The student is warned against using such factors before he is *perfectly familiar* with the method of calculating out the correction for himself. Such a table is not intended to save him the trouble of *learning* how to make the necessary calculations, but only to save the time and trouble of continually repeating the same rather lengthy calculations when he *does* know how to make them.

until the air has been entirely swept out. The upper tap is then closed, and the lower one turned so as to re-establish communication with the pressure-tube.

When the available supply of the gas is comparatively small, it may be collected in a glass tube over water (or, if necessary, over mercury), and afterwards transferred to the burette as described below. The tube may conveniently have the form shown in Fig. 79. It is first filled with water by sucking the liquid up and

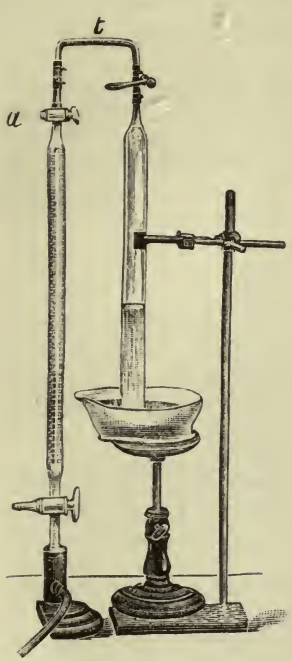

Fig. 79.

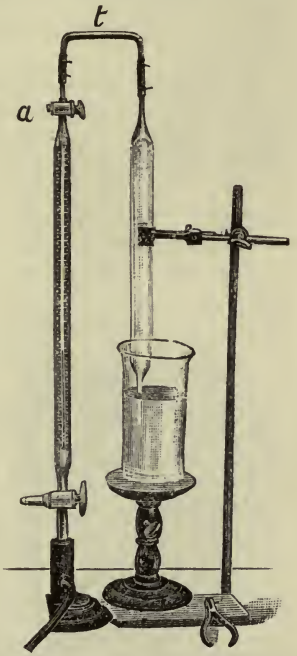

Fig. 80.

closing the rubber with a pinch-cock, and the gas is then passed up from below in the usual manner. The tube is then connected to the gas burette, with the same precautions against enclosing air in the joints as given below.

When the gas is collected away from the laboratory, it should be taken in glass tubes drawn out to a capillary constriction at each end. These tubes are filled either by aspirating the gas

through them so as to sweep out the air, and then hermetically sealing them at the constrictions; or by taking them to the spot in a vacuous and sealed condition, and then breaking open one end in the gas to be collected. After the gas has filled the tube, the end is again hermetically sealed.

In order to transfer the gas from the sealed tube to the burette, a piece of capillary tube, *t*, bent twice at right angles, is attached to the latter, as shown in Figs. 79 and 80, the joints being wired round. The pressure-tube is then raised, until water completely fills the measuring-tube and drops from the open end of the bent capillary.*

Near to each end of the sealed tube, a slight scratch with a file is made. Over one end a short piece of rubber tube is slipped, and the projecting portion of it filled up with water. The bent capillary (already entirely full of water) is then introduced into this tube, and the latter secured with binding wire. In this way all air is excluded from the joint. The lower end of the tube is dipped into a vessel of water.

The tube is broken at the file-mark within the indiarubber joint, and the end beneath the water is broken off by means of a pair of pliers. On lowering the pressure-tube and opening the tap *a* at the top of the measuring-tube, the gas will be drawn over into the burette.

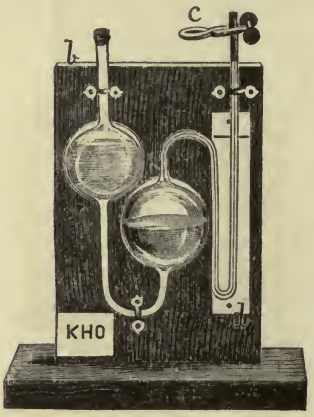

Fig. 81.

Absorption of Gases. — Except when the absorbing liquid is water (in which case the absorption is made in the measuring-tube of the burette), the absorption of the gases in a mixture is carried out in a separate piece of apparatus.

Fig. 81 shows the Hempel gas-pipette, which is employed for this purpose. It consists of two bulbs connected by a bent tube, mounted upon a wooden stand. The capacity of the larger bulb should be at least 150 c.c., so that when the gas from the full

* Whenever the available supply of the gas to be analysed renders such a course possible, the water used in the burette should be first saturated with the gas by shaking a quantity of water with some of the gas in a stoppered bottle for a short time.

burette (*i.e.* 100 c.c.) is transferred to it, there will be room for a considerable quantity of the reagent also. The bent tube *d* has a capillary bore, and a strip of white glass or porcelain is fixed behind it, in order to render the position of the liquid in the tube more visible. Upon the end of this tube a short piece of moderately stout rubber tube is secured with wire, and the tube furnished with a pinch-cock. The pipette is filled by pouring the reagent through the rather wide tube *b* (for which purpose a thistle-funnel should be used, so as to avoid spilling the reagent over the outside), the clamp *c* being open. Such a volume of the reagent is introduced, that when it is sucked up into the capillary tube nearly to the top, there shall be just a small quantity of the liquid in the smaller bulb.

When not in use, the tube *b* should be closed with a small cork, the rubber tube being closed, not with the pinch-cock (which spoils the tube after a time), but by inserting a short piece of glass rod into the tube.

A separate pipette is used for each reagent, and they should be distinctly labelled so as to indicate the reagent they contain.

In cases where it is necessary to guard the reagent from contact with the atmosphere (as, for example, with alkaline pyrogallol, cuprous chloride, etc.), the double pipette shown in Fig. 82 is employed. It differs from the simple pipette only by the two extra bulbs *b*, *b'*, which, by being partially filled with water, serve as a guard or water-seal.

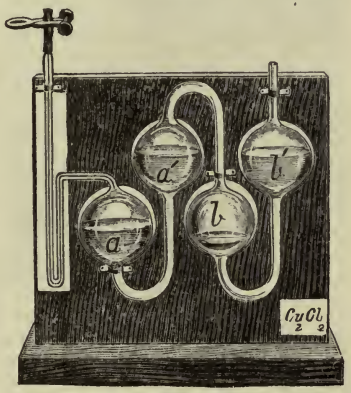

Fig. 82.

This simple addition to the pipette, however, makes it somewhat more difficult to fill. It is necessary so to arrange matters that when the absorbing reagent fills the bulb *a*, the water shall occupy bulb *b*, so that when the reagent passes up into *a'*, the water shall be driven into *b'*. If this condition is not properly secured, as the reagent is made to pass backwards and forwards between *a* and *a'*, either air will be drawn in through the water in the water-seal, or else some of the water itself will be drawn over into *a'*. The following is the best method of filling the apparatus :—

The empty pipette is supported in an inverted position, and an ordinary 10-c.c. pipette is connected to the capillary tube, in the manner shown in Fig. 83. To the free end of the latter a piece of narrow glass tube, *t*, is attached by means of a rubber union provided with a pinch-cock. A short length of rubber tube, also carrying a pinch-cock, is attached to the other end of the gas-pipette. The air within the apparatus is then swept out by passing a stream of some inert gas (*i.e.* inert towards the particular reagent which is destined to fill the pipette), such as nitrogen, or carbon dioxide. The narrow glass tube is then dipped into the bottle containing the reagent in question, which is drawn up into the apparatus by applying suction through the rubber tube *s*. As soon as the bulb *a* is completely filled (*care being taken not to draw any of the liquid over into bulb a'*), the clamps *c* and *c'* are closed, and the tube *t* disconnected. The apparatus is then turned over into its normal position, the little pipette P being supported by the hand.

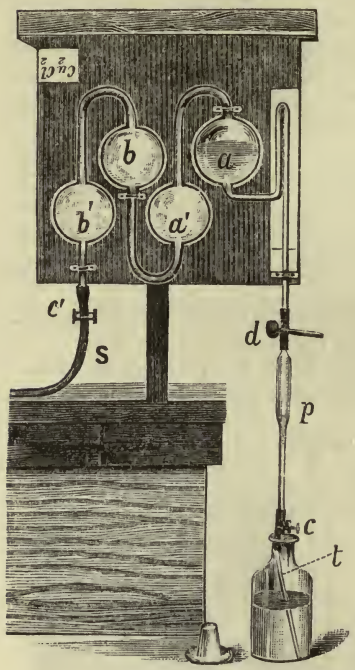

Fig. 83.

The burette (which has previously been filled with the same inert gas used for the pipette) is now attached to the rubber union at *c* by means of the bent capillary tube, as shown in Fig. 84. The reagent should now occupy the entire space between the clamp *c*, and a point *x* in the bent tube, except probably for a small bubble which will have collected at *y*.

The rubber tube S is now removed, and 3 or 4 c.c. of water are introduced into the bulb *b'* by means of a thistle funnel. This water will partly descend into the bent tube uniting *b'* with *b*, and is intended to serve as the temporary water-seal.

The inert gas in the burette is now slowly passed into the pipette by raising the pressure-tube and opening the tap of the measuring-tube and the clamps *c* and *d*. As the gas passes in, the reagent is driven from bulb *a* to *a'*, while the gas which was in *a'* is expelled through the small quantity of water in *b'*. When the

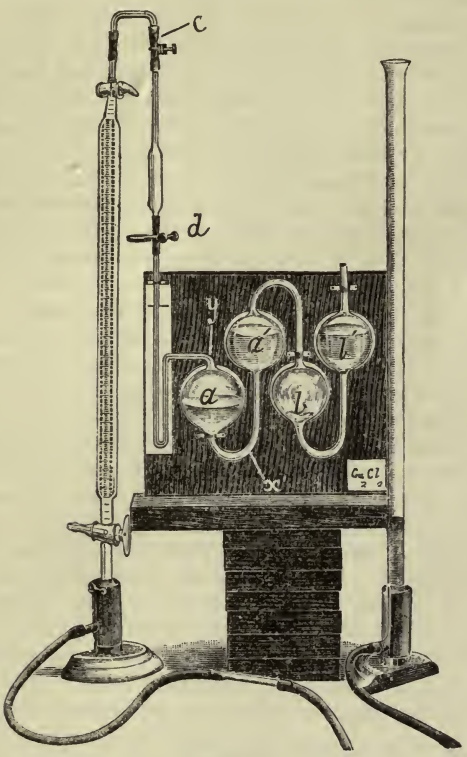

FIG. 84.

whole of the gas from the burette has been transferred to the pipette, clamp *c* is closed, and water is introduced into the bulb *b'* until it is nearly filled.

The clamp *d* is now closed, and the little pipette removed. The clamp should be opened again just to allow the liquids to sink to their natural level, and the rubber then closed by means of a

plug of glass rod. The gas-pipette is now properly charged, the space between the reagent and the water-seal being occupied by inert gas, while the confining water occupies such a position in the bulbs *b* and *b'* that it will neither pass over into *a'*, nor allow air to pass through when the reagent is being transferred backwards and forwards from *a* to *a'*.

The interposition of the 10-c.c. pipette in the filling operation will have secured the introduction of rather more than enough of the reagent to fill the bulb *a*. When, therefore, in the process of returning a gas from the absorption-pipette to the burette, the reagent completely fills the bulb *a* and the capillary tube, there will still remain a few cubic centimetres in bulb *a'*.

Since 100 c.c. of gas (the capacity of the burette) may at any time be introduced into bulb *a*, it will be evident that the capacity of *a'*, *b*, and *b'* must not be less than this volume, otherwise they will overflow. Badly blown specimens are sometimes met with which have this defect; it will be at once discovered during the operation of filling, and the apparatus must be rejected.

Gases commonly estimated by Direct Absorption.—The gases which are most commonly estimated by simple absorption in a gas-pipette, and the reagents that are employed for the purpose of their absorption, are the following :—

(1) **Carbon dioxide;** absorbed by **potassium hydroxide.** The reagent is made by dissolving 150 grams of commercial caustic potash in 500 c.c. of water, and is used in the simple two-bulb pipette.

(2) **Carbon monoxide;** absorbed by **cuprous chloride.** Cuprous chloride is soluble both in ammonia and in hydrochloric acid, and a solution in either solvent may be employed for the absorption of carbon monoxide (see footnote, p. 86). The acid solution is preferable, however, except under the circumstances described on p. 408, when the ammoniacal solution must be used.

(*a*) *Acid Solution.*—Thirty grams of cuprous chloride* are

* Cuprous chloride is supplied by the dealers in a fairly pure state. Should the student require to prepare it for himself, it may readily be obtained by dissolving 25 grams of copper oxide in 200 c.c. of strong hydrochloric acid, and adding about 25 grams of copper clippings or wire. The mixture is then gently boiled for about an hour, more acid being added if the solution becomes much reduced in bulk by evaporation. The dark solution is then poured into a large beaker of water, and the white precipitate of cuprous chloride allowed to settle. The clear liquid is decanted off, and the precipitate transferred to a flask or bottle, where it is again allowed to settle and the liquid poured off. Hydrochloric acid (strong acid 3 parts, water 1 part) is then added in sufficient quantity just to dissolve the cuprous chloride. A few strips of copper are introduced, and the flask or bottle closed with a good cork (a glass stopper should not be used).

mixed with 50 c.c. of water in a ¼-litre flask, and 150 c.c. of strong hydrochloric acid added. If a few copper turnings or thin strips of the metal be put into the brownish solution, and the flask corked up and left for a day or so, the liquid will become colourless.

(*b*) *Ammoniacal Solution.*—Twenty grams of cuprous chloride are mixed with 150 c.c. of water in a flask fitted with a cork carrying two tubes, one reaching to the bottom, while the other ends just below the cork. The air is swept out of the flask by a stream of indifferent gas (hydrogen or carbon dioxide), after which the exit tube is made to dip beneath water. A stream of ammonia is then passed into the solution (obtained by gently heating a strong solution of ammonia in a separate flask, the latter not being connected until the issuing ammonia has expelled the air) until the cuprous chloride has entirely dissolved. Any unnecessary excess of ammonia should be avoided. This reagent is used in the double pipette, and must be exposed to the air as little as possible during the process of filling the pipette.

(3) **Oxygen;** absorbed by **alkaline pyrogallol.*** The reagent is prepared by dissolving 20 grams of pyrogallol in 200 c.c. of the potassium hydroxide solution described above (No. 1).

This reagent is used in the double pipette.

Should the sample of gas under analysis contain more than about 25 per cent. of oxygen (which is seldom the case), it should be diluted with a known volume of hydrogen until the proportion of oxygen is reduced to within this amount; otherwise the traces of carbon monoxide which are liberated during the absorption of oxygen by alkaline pyrogallol will prejudice the result. If the original gas, however, is known to contain no carbon monoxide, this difficulty may be obviated by transferring the gas, after absorption in the pyrogallol, to the pipette containing cuprous chloride.

(4) **Hydrocarbons** (olifines); absorbed by **fuming sulphuric acid.** This reagent is used in the single pipette.

The same hydrocarbons may also be absorbed by **bromine Water,** prepared by saturating water with bromine. After exposure to either of these reagents, the gas is freed from sulphur dioxide or from the vapour of bromine by being transferred to the caustic potash pipette. The tubes of the pipette containing the fuming sulphuric acid must be closed by means of a piece of glass rod and rubber tube when the apparatus is not in use.

Benzene vapour is absorbed by fuming sulphuric acid, but not by bromine water. It is also absorbed by fuming nitric acid.

* Sometimes, but incorrectly, called "pyrogallic acid."

(5) **Nitric oxide;** absorbed by **ferrous sulphate.**—The solution of ferrous sulphate is prepared by dissolving 70 grams of the salt in 150 c.c. of water. It is used in a double pipette.

[Potassium permanganate acidified with sulphuric acid may also be used for the absorption of nitric oxide; in this case the simple pipette is employed.]

(6) Chlorine, sulphuretted hydrogen, sulphur dioxide, hydrochloric acid, and acid gases generally, may be absorbed from gaseous mixtures by caustic potash.

Estimation of Carbon Dioxide, Oxygen, Carbon Monoxide and Nitrogen.—As a first exercise in manipulating the gas-apparatus, an absorption-analysis may be made of an artificially prepared mixture of these four gases, most of which are very constantly met with associated together in such gaseous mixtures as furnace gases, generator gases, water-gas, coal-gas, etc.

The mixture may be prepared by partially filling (say about three-fourths) the collecting-tube shown in Fig. 79, p. 391, with air. A small quantity of crystallised oxalic acid is heated with strong sulphuric acid in a test-tube fitted with a cork and delivery-tube, and the mixed oxides of carbon collected in the tube so as to fill the remaining one-fourth. The tube now contains the four gases in question.

They will be estimated by absorption in the following order: *—

(1) Carbon dioxide; absorbed by caustic potash.
(2) Oxygen; absorbed by alkaline pyrogallol.
(3) Carbon monoxide; absorbed by cuprous chloride.
(4) Nitrogen; estimated by difference.

(1) **Saturating the Water for the Burette.**—A stoppered bottle of about 300 c.c. capacity is filled with water and inverted in a water-trough. About 100 c.c. of the gaseous mixture is bubbled up into the bottle, which is then closed with the stopper, and the gas thoroughly shaken up with the remaining water for a few minutes.

Some of this water (now saturated with the gas to be analysed) is poured into the pressure-tube, and the tap at the foot of the measuring-tube is turned so as to establish communication between the two tubes. (This tap is not again touched throughout the analysis, the passage of the gas to and from the measuring-tube

* It will be obvious that the *order* in which the gases are to be absorbed from a mixture must be carefully considered. Thus, in the above illustration the oxygen must be absorbed *before* the carbon monoxide, otherwise the reagent used to remove the latter gas would be acted upon by the oxygen present (see p. 86).

and the various pipettes being controlled entirely by the upper tap.)

The bent capillary connecting-tube is then attached to the top of the measuring-tube, and the latter is completely filled with water by raising the pressure-tube and opening the tap at the top, until the liquid drips from the end of the capillary tube. The tap is then closed. The indiarubber connector upon the collecting-tube containing the gas is filled up with a drop of water, and then joined to the end of the bent capillary (see Fig. 79, p. 391), and the connections secured with wire. The pressure-tube is lowered, and the pinch-cock upon the collecting-tube and the upper tap of the measuring-tube are opened, whereby gas is drawn over into the latter tube. When sufficient gas has thus been transferred, the pinch-cock and tap are closed, and the two tubes disconnected. One minute is allowed to elapse for the water to drain down the walls of the measuring-tube, when the volume of the gas introduced is read off by lowering the pressure-tube until the level of the water in it and in the measuring-tube is the same. The graduation mark which coincides with the bottom of the meniscus represents the volume of gas taken for the analysis.*

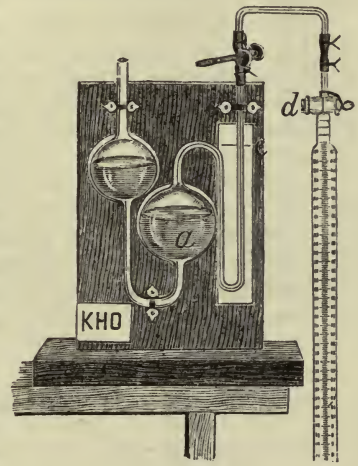

FIG. 85.

(2) **Estimation of Carbon Dioxide.**—The burette is now attached to the absorption pipette containing caustic potash in the manner shown in Fig. 85. Before the two pieces of apparatus are thus united, the potash solution is drawn up so as to completely fill the bulb *a*, and the bent capillary tube to the mark *c*, which is made upon the white tablet. The pinch-cock keeps it in this position. After the rubber connections have been secured with

* It is convenient, when possible, to employ 100 c.c. of the gas under analysis, in which case the number of cubic centimetres of the various constituents which are absorbed, represents the percentage of each ingredient in the gas mixture. If, therefore, more than 100 c.c. has been first introduced into the apparatus, the excess may be removed by raising the pressure-tube until the gas is compressed to exactly 100 c.c.; then, keeping the water in that

wire, the pinch-cock is opened, when, if the joints are tight, the reagent will not sink from its position at *c*. The pinch-cock may be kept open by raising it so that it nips the glass tube.

The pressure-tube is now raised (being handled exclusively by the foot), and the tap *d* at the top of the measuring-tube is opened. The gas is thus transferred completely to the bulb *a* of the pipette. Two or three drops of water from the measuring-tube are allowed to follow the gas into the bulb (by so doing the capillary tube of the pipette is *washed* each time the apparatus is used), after which the tap *d* is closed.

The gas is allowed to remain in contact with the potash for about five minutes, during which time the apparatus is gently shaken so as to moisten the sides of the bulb with the reagent.

The pressure-tube is then lowered, and tap *d* opened, whereby the gas is returned to the measuring-tube. As soon as the potash reaches the point in the capillary tube opposite the mark *c*, the tap is closed.

On no account must the reagent be allowed to reach the rubber connection, or to pass over into the measuring-tube.

The pressure-tube is then held in such a position that the water stands at the same level as in the measuring-tube, and, after waiting a minute for the water to drain down the walls of the tube, the volume is read off.

In order to be sure that the absorption of the carbon dioxide has been complete, the gas is transferred once more to the pipette, and gently shaken with the potash as before, after which it is again returned to the measuring-tube, and its volume read off at atmospheric pressure, allowing the same interval for the water to run down. If the two readings agree, the first absorption was complete.*

Original volume of gas	... ...	100 c.c.
Volume after absorption by potash	...	88 ,,
Carbon dioxide	... ...	12 ,, = **12 per cent.**

position by pressing a finger upon the rubber tube, the tap at the top of the measuring-tube is momentarily opened. This lets the excess of gas escape, leaving 100 c.c. at atmospheric pressure. This is controlled by again lowering the pressure-tube until the water in each tube is at the same level, when the gas should be found to occupy 100 c.c.

* If due care be taken to avoid handling the apparatus, except by the foot of the pressure-tube, the temperature of the gas will not undergo any material alteration during the course of an analysis. The temperature may be watched by suspending a thermometer in the water in the pressure-tube, as explained on p. 388.

(3) **Estimation of the Oxygen.**—The potash pipette is detached from the bent capillary tube at the joint immediately above the pinch-cock, Fig. 85, and replaced by the double pipette containing the alkaline solution of pyrogallol. Before the latter is connected, the reagent is drawn up into the capillary tube to a marked point, which is as nearly as possible the same distance from the pinch-cock as that upon the previous pipette. The gas is transferred to the pipette for absorption exactly as in the former case, and is left in contact with the reagent, with occasional gentle shaking, for ten minutes. It is then returned to the measuring-tube, the same care being taken to bring the reagent *exactly* to the mark upon the capillary tube. The tap is closed, and, after allowing time for the water to drain off the walls of the measuring-tube, the volume of the residual gas is read off at atmospheric pressure.

Volume of gas before absorption of oxygen	88 c.c.
„ „ after „ „	73 „
Oxygen	15 „ = **15 per cent.**

(4) **Estimation of the Carbon Monoxide.**—The pyrogallol pipette is disconnected and replaced by the one containing cuprous chloride in acid solution, the reagent being previously drawn over into the capillary tube to a mark in the same relative position as in the previous cases.

The gas is transferred to the pipette and allowed to remain exposed to the reagent for ten minutes; after which it is returned to the measuring-tube, and its volume determined with the same precautions as before.

Volume before absorption of carbon monoxide	73·0 c.c.
Volume of residual gas (nitrogen) ...	60·5 „
Carbon monoxide absorbed ...	12·5 „ = **12·5 per cent.**

Hence the composition of the mixture under analysis is—

Carbon dioxide	12·0
Carbon monoxide...	12 5
Oxygen	15 0
Nitrogen (by difference)	60·5
	100·0

A second analysis of the same mixture should be made.

III. Estimation by Combustion.

Hydrogen.—When hydrogen and oxygen combine, according to the equation—

$$2H_2 + O_2 = 2H_2O$$

the two volumes of hydrogen and one volume of oxygen practically cease to occupy space, since the volume of the condensed water is inappreciable. By measuring the shrinkage or contraction which takes place under these circumstances, and multiplying this by $\frac{2}{3}$, the volume of hydrogen which was burnt is ascertained.

In order, therefore, to estimate hydrogen, a measured volume of the gas is mixed with a measured volume of air—rather greater than is required to furnish the necessary amount of oxygen—and the mixture of hydrogen and oxygen caused to unite by one of the methods described below. After the combination the residual gas is measured, when two-thirds of the contraction will represent the volume of the hydrogen consumed.

Two methods are here given for bringing about the combustion of the mixture of oxygen and hydrogen.

(*a*) **Combustion of Hydrogen by means of Palladiumised Asbestos.**

Epitome of Process.—The hydrogen is mixed with the necessary excess of air in a gas-burette, which is attached to an absorption-pipette charged only with water. The capillary attachment between the two pieces of apparatus contains a thread of asbestos, upon which has been deposited a quantity of finely divided palladium. As the gas is transferred slowly from the burette to the pipette, it passes over this palladiumised asbestos (which is gently warmed by a small flame), and the oxygen and hydrogen are thereby caused to unite. The gas is finally returned to the burette and measured.

As an exercise in the process, a mixture of pure hydrogen and air may be employed. About 20 c.c. of hydrogen, as pure as possible, are introduced into the gas-burette, and the volume measured. The pressure-tube is then lowered, and a quantity of air drawn into the apparatus until the total volume is about 80 or 85 c.c.; that is to say, from 60 to 65 c.c. of air are introduced, and the volume is again exactly measured.

The gas-burette is then attached to a gas-pipette charged with water, by means of the capillary combustion-tube containing the palladiumised asbestos * instead of the usual connecting-tube. The

* The little tube is prepared in the following manner: 0·25 gram. of palladium foil is dissolved in the minimum quantity of *aqua regia* in a small porcelain dish, and the solution evaporated to dryness on a steam-bath. The residue is

palladium is gently heated by brushing a Bunsen flame along the tube, which must be kept warm during the whole operation, so as to prevent water (the product of the combustion) from condensing in it. The temperature of the tube must not approach a visible redness.

The gas is allowed to pass slowly over the warm palladium, which will be seen to glow at the end towards the incoming gas. When the whole of the gas has been transferred to the pipette, it is drawn back again into the burette. This process is repeated once or twice (if the palladiumised asbestos is in good order, one repetition of the operation usually completes the combustion), after which the residual gas is measured. It is then passed once more into the pipette and back, and measured again. If the two measurements agree, the process is complete.

EXAMPLE.—Original volume of hydrogen (by electrolysis) = 20·5 c.c.

Excess of air added. Total volume of mixture ...	83·8 c.c.
Volume after combustion	53·2 „
Therefore contraction	30·6 „

$30{\cdot}6 \times \frac{2}{3} = \mathbf{20{\cdot}4}$ c.c. = volume of hydrogen found

moistened with three or four drops of strong hydrochloric acid, added from a dropping-tube, and 20 drops (1 c.c.) of water added. The mixture may be gently warmed to complete the solution. To this red-brown solution, when cold, 20 drops of a cold saturated solution of sodium formate are added.

Into this mixture, which will not exceed 2·5 c.c. in volume, 0·25 gram of asbestos thread is immersed, which will soak up the whole of the liquid.

[This thread must be sufficiently fine to admit of being pushed into a capillary tube of 1 mm. bore. It may be obtained by unravelling a piece of asbestos cloth so as to get single strands. It is cleansed from grease by treating it once or twice with a little warm carbon disulphide in a test-tube, and then spreading it out on a clean piece of paper to dry; after which it should be heated for a few minutes on a piece of platinum foil. A quarter of a gram of this thread will be about 60 cms. in length.]

A strong solution of sodium carbonate is added by means of a dropping-tube, and gently worked into the soaked thread with a glass rod, until the mixture is alkaline, and the dish placed upon a steam-bath. A gentle heat suffices to reduce the palladium, which is then precipitated throughout the asbestos as a black deposit. When the contents of the dish are dry, they are rinsed three or four times with hot water in order to dissolve out the soluble salts. The thread is then removed, and cut into short pieces about 4 cms. long. One of these pieces is straightened out with a gentle twisting of the fingers, and laid upon a piece of blotting-paper for a few minutes to remove the superfluous water. It is then introduced into a piece of thick-walled capillary tube, 1 mm. bore and about 15 cms. long. When the thread has been pushed a little way into the tube, it may readily be drawn into the middle by applying a gentle suction to the other end. The thread is then dried by gently warming the tube and slowly drawing air through it, after which the tube is bent at right angles, about 3 cms. from each end. The same piece of palladiumised asbestos may be used for several combustions.

(*b*) **Combustion of Hydrogen by Explosion with Air.**—For this purpose the mixture of hydrogen with excess of air is transferred to a special "explosion-pipette," in which are sealed two platinum wires, whereby the gaseous mixture may be ignited by a spark from a Ruhmkorf coil.

Fig. 86 shows a form of explosion-pipette in which the gas is confined over water.* Water which has been acidulated with sulphuric acid, and boiled to expel dissolved gases, is introduced at *a* until the bulb *b* is just full, and the liquid stands level in the other limb. Upon the tubes *a* and *e*, pieces of thick-walled rubber tube are securely wired, and a pinch-cock is placed on each.

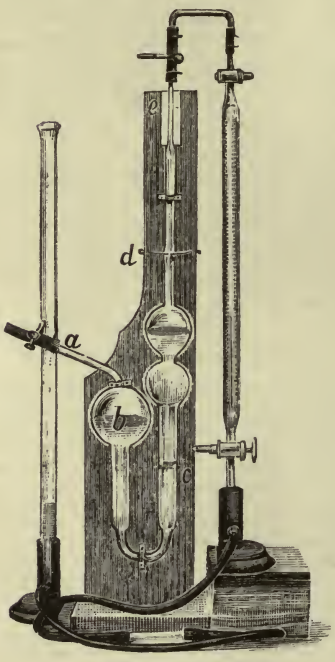

Fig. 86.

At *d* two platinum wires are sealed into the glass, between which the electric spark is passed when the gas is to be fired.† In the lower part of the tube, at *c*, two platinum electrodes are fused into the glass. These are for the purpose of adding a small quantity of "electrolytic gas" to the mixture, when the proportion of combustible gas is so small that no explosion will take place when the electric spark is passed. Before the "electrolytic gas" is generated, the mixture under analysis is transferred to the measuring-tube, which is then detached from the "explosion-pipette." The two wires from the *battery* (not from the coil) are then connected to the electrodes (*c*), and the oxygen and hydrogen which are evolved are allowed to escape.

* Another form of explosion-pipette, in which mercury is the confining liquid, is shown and described on p. 407.

† To prevent the loops of these thin wires from being broken off, it is well to attach to each a short piece of stouter platinum wire, and pass these through holes in the wooden support so that their ends project and can be bent over into loops, as shown in the figure. The same may be done for the wires at *c*.

The current is allowed to pass for about fifteen minutes, in order to saturate the water, after which the current is stopped and the liquid driven up to the usual mark upon the capillary. The burette is reconnected, and the gas returned to the pipette. A small quantity of electrolytic gas is then generated (the amount depending upon circumstances), and thoroughly mixed with the gas already present, before exploding. It is not necessary to know the *volume* of the gas thus added, since it entirely disappears when fired.

As a first exercise, a mixture of pure hydrogen and air may be exploded. About 10 to 15 c.c. of hydrogen are introduced into the gas-burette, and after being exactly measured, about 60 to 70 c.c. of air are added, and the mixed gases again measured. The burette is then attached to the explosion-pipette, the liquid in the latter being previously drawn up to a mark upon the capillary tube *e*.

The gas is then passed over into the pipette, and the clamps upon the rubber tubes both closed. The wires from the induction coil are attached to the wires at *d*, and the electric spark allowed to pass. The explosion, although not at all violent, will cause a momentary expansion within the apparatus, but if sufficient liquid is present, no gas will be driven out of the bulb-tube. The thick rubber tube upon *a* being closed, the small quantity of air which is enclosed in the bulb *b* serves as a cushion or "buffer" at the moment of explosion, and thus relieves the other part of the apparatus from undue pressure.

The moment after passing the spark, the tube upon *a* is opened; and then the gas is returned to the burette and measured. The contraction represents the hydrogen and the atmospheric oxygen with which it has combined to form water, and two-thirds of this shrinkage is the volume of hydrogen which was present.

EXAMPLE.—Volume of hydrogen taken = 12·5 c.c.

Volume of hydrogen and air	...	...	...	75·8 c.c.
Volume after explosion	...	...	...	57·5 „
Contraction	...	...	...	18·3 „

$18{\cdot}3 \times \frac{2}{3} = 12{\cdot}2$ c.c. = volume of hydrogen found

For practice in the use of "electrolytic gas," the following experiment may be made: A quantity of air (about 60 c.c.) is introduced into the burette, and its volume measured in the usual way.

The current from four or five Grove's cells (or its equivalent from any other convenient source) is passed through the dilute acid in the explosion-pipette by means of the electrodes at *c* (Fig. 86) for

about ten minutes, and the liquid shaken up once or twice with the gas, in order that it may become saturated. The current is then interrupted, and the liquid drawn up to the mark upon the capillary. The burette containing the measured volume of air is then attached in the usual manner. About 12 c.c. of electrolytic gas are then generated in the pipette, and drawn over into the burette.* The mixture of air and electrolytic gas is then passed twice backward and forward from the burette to the pipette, in order to ensure their complete admixture, after which the clamps are closed, and the mixture fired. The residual gas is transferred to the burette and measured, when the volume should be the same as that of the air originally introduced.†

Methane (*Marsh-gas*).—When a mixture of methane and air, or oxygen, is exploded, carbon dioxide and water are formed; and from the following equation :—

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

it will be seen that methane, when burnt, gives *its own volume* of carbon dioxide; and also that three volumes of mixed gases shrink to one volume (*i.e.* the 1 volume of CO_2), since the water ceases to occupy space. The contraction, therefore, is two-thirds of the total volume of the reacting gases; or, in other words, the contraction is equal to twice the carbon dioxide produced, or twice the volume of the marsh-gas burnt.

Owing to the effect of pressure in increasing the solubility of carbon dioxide in water, it is only possible to obtain accurate results when mercury is used as the confining liquid.‡ An explosion-

* The actual amount of electrolytic gas which has been added may be ascertained by measuring the total volume of gas now in the burette. It is not necessary, however, to know this volume exactly, and a very little experience will enable the operator to judge of the volume by the space it occupies in the explosion-pipette as it is generated.

† Usually after the *first* experiment the volume of the residual air is not *quite* identical with that which was originally taken, owing to the imperfect saturation of the liquid with the various gases. If this is the case, a similar quantity of electrolytic gas should be again added, and the mixture fired once more after thorough admixture. The volume of the residual gas after this second explosion should then exactly agree with that which was measured after the first operation. The process may be repeated with varying amounts of electrolytic gas, and the volume of the residue will be found to remain constant.

‡ With a view to ascertain the extent of the loss of carbon dioxide by solution in water when the explosion is conducted over that liquid, the following experiments were made with the apparatus figured on p. 404 :—

(1) 67 c.c. of a mixture of air and carbon dioxide, containing 9 per cent. of CO_2, were introduced into the apparatus, and 12 c.c. of electrolytic gas added. After explosion, the volume remaining occupied 66·7 c.c.

Loss of CO_2 = 0·3 c.c. = 0·4 per cent.

pipette in which mercury is employed is shown in Fig. 87. It differs from the ordinary absorption-pipette only in containing two platinum wires, fused into the upper part of bulb *a*, and in being furnished with a stopcock, in order to close the communication between the two bulbs.

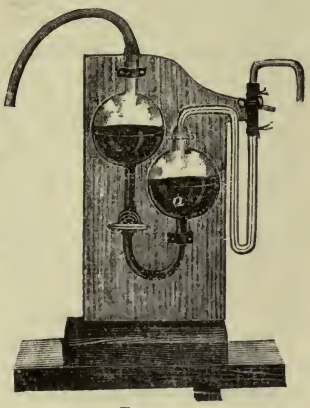

FIG. 87.

Before the apparatus is connected to the burette containing the measured mixture for explosion, the mercury is driven over into the capillary tube, to a fixed mark,* by blowing through the rubber tube upon the upper bulb; and similarly, when the gas is transferred from the burette to the explosion-pipette, it must be drawn over by applying suction to the same rubber tube. The water from the burette should be made to follow the gas so as to *just* fill the capillary tube, but without allowing any to enter the bulb. Before firing the mixture, the pinch-cock and the tap are closed.

(2) 78 c.c. of a similar mixture, containing 20 per cent. CO_2; 15 c.c. electrolytic gas added. Volume after explosion = 77·2 c.c.

Loss of CO_2 = 0·8 c.c. = 1·0 per cent.

(3) 50·8 c.c. of similar mixture, containing 40 per cent. CO_2; 15 c.c. electrolytic gas added. Volume after explosion = 49 c.c.

Loss of CO_2 = 1·8 c.c. = 3·3 per cent.

About the same volume of electrolytic gas was added three times, and the mixture exploded and measured after each addition; the volumes obtained were 47·4 c.c., 46·2 c.c., and 45·2 c.c., showing a fairly regular loss of carbon dioxide.

(4) 47·2 c.c. of air, containing 36·4 per cent. CO_2

(*a*) 20 c.c. electrolytic gas added; after explosion, volume = 45·6 c.c.
(*b*) 12 ,, ,, ,, exploded again, volume = 45·0 ,,
(*c*) 20 ,, ,, ,, ,, ,, volume = 43·6 ,,

(*a*) loss = 1·6 c.c., or 3·4 per cent.
(*b*) loss = 0·6 ,,
(*c*) loss = 1·4 ,,

Experiments 1, 2, and 3 show that, with about the same force of explosion, the loss of CO_2 increases as the percentage present rises; while Experiment 4 shows that, with the same percentage of carbon dioxide, the amount absorbed depends upon the force of the explosion.

* In the apparatus here figured, the capillary tube is enamelled white on the back, like the stem of a thermometer; in other specimens the tube is of clear glass, with a white tablet fixed behind, as in Figs. 81, 82.

After the explosion, the gas is transferred to the burette and measured. The explosion-pipette is then disconnected and replaced by the simple absorption-pipette containing caustic potash, and the carbon dioxide absorbed in the usual way.

Mixtures of Hydrogen, Methane, and Nitrogen.—Many gaseous mixtures which constantly come under analysis (such as coal-gas, producer gas, water-gas, blast-furnace gases) contain varying quantities of these three gases along with others. After all the other gases have been estimated by absorption in their respective reagents, the hydrogen and marsh-gas in the residue are determined by one of the two following methods, while the nitrogen is estimated by difference :—

(*a*) The gas is mixed with an excess of air, and the hydrogen estimated by combustion by means of palladiumised asbestos (p. 402). Under these conditions, the marsh-gas does not burn.

The marsh-gas is then determined by exploding the residual mixture and absorbing the carbon dioxide, as described above.

The volume of nitrogen is found by deducting from the original volume of gas the hydrogen and marsh-gas thus determined.

EXAMPLE.—One hundred cubic centimetres of coal-gas were exposed to the action of the following reagents—

(*a*) Caustic potash ; to absorb carbon dioxide.
(*b*) Alkaline pyrogallol ; to absorb oxygen.
(*c*) Fuming sulphuric acid ; to absorb olefines and benzene vapour.
(*d*) Ammoniacal cuprous chloride ; to absorb carbon monoxide.*

The residual gas, measuring 86·6 c.c., was returned to the cuprous chloride pipette, while the burette was disconnected and the water in it (previously saturated with coal-gas) was replaced by water saturated with air.

Twenty cubic centimetres of the gas were transferred to the burette (the rest being reserved for a subsequent experiment), and air added in more than sufficient quantity for the complete combustion of the hydrogen.

Volume of gas = 20·0 c.c.
volume of gas + air = 64·4 „

This mixture was then passed over the palladiumised asbestos (p. 402).

* When the absorption of carbon monoxide is to be followed by the combustion of hydrogen with palladiumised asbestos, the ammoniacal solution of cuprous chloride should be used.

Volume after combustion of hydrogen = 48·2 c.c.
therefore 64·4 − 48·2 = 16·2 „ = contraction
and 16·2 × $\frac{2}{3}$ = **10·8** = volume of hydrogen in 20·0 c.c. of gas

To the residual gas (consisting of marsh-gas, nitrogen, and a small surplus of oxygen) an excess of oxygen was added.

Volume of residual gas = 48·2 c.c.
volume of residual gas + oxygen = 69·6 „

The mixture was then exploded, and the carbon dioxide absorbed.

Volume after explosion = 52·8 c.c.
therefore 69·6 − 52·8 = 16·8 = contraction
volume after absorption of CO_2 = 44·4
therefore 52·8 − 44·4 = 8·4 c.c. = volume of CO_2 produced
and therefore **8·4** c.c. = volume of marsh-gas in 20 c.c. of gas
20·0 c.c. − (10·8 + 8·4) = 0·8 c.c. = volume of nitrogen in 20 c.c.

Since the original volume of gas taken for analysis was 100 c.c.—

then $\frac{10{\cdot}8 \times 86{\cdot}6}{20}$ = 46·46 = per cent. of hydrogen

and $\frac{8{\cdot}4 \times 86{\cdot}6}{20}$ = 36·07 = per cent. of marsh-gas

and $\frac{0{\cdot}8 \times 86{\cdot}6}{20}$ = 3·46 = per cent. of nitrogen

(*b*) By this method the mixture of hydrogen, marsh-gas, and nitrogen is mixed with air or oxygen sufficient for the complete combustion of both the combustible gases, and the mixture exploded. The contraction is then measured, after which the carbon dioxide is absorbed and the volume again measured. From these data the volumes of the hydrogen and marsh-gas can be calculated. As already explained, p. 406, the contraction due to the combustion of marsh-gas is twice the volume of carbon dioxide; if, therefore, the volume of carbon dioxide is ascertained (by absorption with potash), and twice this volume be deducted from the contraction on explosion, the product will represent the contraction due to the combustion of the hydrogen.

Let C = contraction on explosion, and C′ = volume of CO_2 produced (*i.e.* contraction on absorption with potash);

Then C − 2C′ = contraction due to the hydrogen
and $\frac{2}{3}$(C − 2C′) = volume of hydrogen

Again, since the volume of carbon dioxide produced is the same as the volume of marsh-gas burnt—

$$C' = \text{volume of marsh-gas}$$

EXAMPLE.—A portion of the mixture of hydrogen, marsh-gas, and nitrogen employed in the previous example (being the residual gas after the removal of the absorbable constituents from a sample of coal-gas) was measured in the burette, and an excess of air added.

Volume of gas taken = 14·2 c.c.
volume of gas + air = 97·6 „
after explosion, volume = 74·2 „
therefore contraction, C, = 97·6 − 74·2 = 23·4
After absorption by KHO, volume = 68·2 c.c.
therefore C′ = 74·2 − 68·2 = 6

Hence volume of H in 14·2 c.c. of the gas = $\frac{2}{3}(23{\cdot}4 - 12)$ = **7·6** c c.
and volume of CH_4 in 14·2 c.c. of the gas = **6·0** „
and volume of N in 14·2 c.c. of the gas = 14 2−(7·6+6·0) = **0·6** „

Calculating the percentage as in the previous example—

$$\frac{7{\cdot}6 \times 86{\cdot}6}{14{\cdot}2} = \mathbf{47{\cdot}0} \text{ per cent. of hydrogen}$$

$$\text{and } \frac{6{\cdot}0 \times 86{\cdot}6}{14{\cdot}2} = \mathbf{36{\cdot}5} \text{ per cent. of marsh-gas}$$

$$\frac{0{\cdot}6 \times 86\,6}{14{\cdot}2} = \mathbf{3{\cdot}6} \text{ per cent. of nitrogen}$$

In cases where the gas under analysis contains a relatively large proportion of nitrogen; as, for example, in the case of producer gas, or blast-furnace gases, the addition of air would dilute the gas to such an extent as to render it non-combustible. Under these circumstances, therefore, either oxygen must be substituted for air, or else, after sufficient air has been added to furnish the requisite amount of oxygen, a few cubic centimetres of electrolytic gas may be added to the mixture. The electrolytic gas for this purpose may be generated in the pipette described on p. 404, and then transferred to the mercury explosion-pipette.

The Nitrometer.

Many simple processes of gas estimations (such as when it is only desired to determine one gas by absorption) are conveniently and quickly performed by means of the Lunge nitrometer.* This

* So called because originally designed by Lunge, for the estimation of nitrogen oxides in "nitrous vitriol."

consists of a calibrated measuring-tube, *m* (Fig. 88), connected by means of stout rubber tubing to the pressure-tube *p*. By means of the two-way tap upon the measuring-tube, communication can be established at will either with the bent capillary tube *t* or the little reservoir *n*. Mercury is usually employed as the confining liquid.

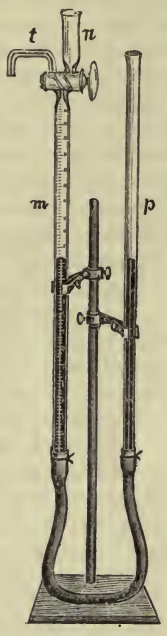

FIG. 88.

To introduce the gas, the pressure-tube is raised until the measuring-tube is completely filled with mercury. The capillary tube *t* is connected to the supply of the gas, and the two-way tap turned so as to open communication between the measuring-tube and the capillary, as seen in the figure, and the gas drawn over by lowering the pressure-tube. By turning the tap one quarter of a revolution, communication with both the exits is cut off.

The absorbing reagent is poured into the reservoir *n*, and introduced into the measuring-tube by first slightly lowering the pressure-tube, and then gently turning the tap so as to open communication between *m* and *n*.*

Besides simple absorption operations, this apparatus is suitable for the estimation of the volume of gas which is evolved in certain definite chemical reactions. These processes are sometimes spoken of as *gas-volumetric* analysis. The following are typical examples :—

(1) The estimation of nitrates, either in commercial nitre, or in the residue obtained on evaporating water for the determination of the nitrates and nitrites.

This process depends upon the fact that when a nitrate is decomposed by strong sulphuric acid in the presence of mercury, this metal is acted upon by the liberated nitric acid with the evolution of nitric oxide. The nitric oxide is therefore the measure of the nitric acid or the nitrate present. One cubic centimetre NO measured at N.T.P. represents 0·00452 gram of KNO_3 or 0·0038 gram of $NaNO_3$.

About 0·1 gram of the nitrate is placed in the reservoir *n*, and dissolved in 2 or 3 c.c. of water. This solution is carefully drawn

* As a safeguard, lest by accident the tap should be turned the wrong way, a rubber connector should be left upon the end of *t*, and closed with a pinch-cock.

into the measuring-tube (previously filled with mercury), and the reservoir rinsed with 1 c.c. of water, which is also allowed to pass into the tube. (With a little experience these operations will be performed without the admission of any air; but should air be drawn in, it may be expelled by raising the pressure-tube slightly, and cautiously opening the tap.) The reservoir is again rinsed by the introduction of 5 or 6 c.c. of strong sulphuric acid, which is followed by the addition of about 10 c.c. more acid. The measuring-tube is then released from its clamp, and the contents carefully shaken by inclining the tube, and then quickly (almost with a jerk) bringing it into the vertical position. In fifteen to twenty minutes the process is complete. The tube is replaced in its clamp and allowed to cool. Before reading the volume of gas, in order to compensate for the column of acid in the tube, a similar volume of acid of the same dilution is poured into the pressure-tube.

(2) By means of a short rubber tube, the tube *t* may be attached to a small flask fitted with a caoutchouc stopper carrying a short glass tube. If in the flask a chemical reaction resulting in the evolution of gas at the ordinary temperature is carried out, the volume of the evolved gas can be measured.

With such an arrangement, the estimation of carbon dioxide in carbonates may be made; also the indirect estimation of manganese dioxide, by measuring the carbon dioxide evolved by the action of the dioxide upon oxalic acid in presence of sulphuric acid, according to the equation—

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2H_2O + 2CO_2$$

Similarly, by the action of hydrogen peroxide upon manganese dioxide, potassium permanganate, or bleaching powder, the oxygen evolved is a measure of the available oxygen in these compounds; half the oxygen given off in each case being derived from the compound, while the other half is from the hydrogen peroxide, as seen by the following equations :—

$$MnO_2 + H_2O_2 = MnO + H_2O + O_2 *$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \dagger$$
$$Ca(OCl)Cl + H_2O_2 = CaCl_2 + H_2O + O_2$$

A weighed quantity of the substance to be tested is introduced into the flask. In the case of manganese dioxide, or potassium permanganate, dilute sulphuric acid is added, but with bleaching

* In the presence of sulphuric acid.

† The importance of ensuring the presence of sufficient sulphuric acid in this and the preceding reaction will be seen from the footnote on p. 54.

powder a small quantity of water only. The reagent (in the above three cases, the hydrogen peroxide) is placed in a test-tube, and deposited within the flask without allowing any of it to come in contact with the materials already present. The rubber cork is inserted in the mouth of the flask, and the apparatus connected to the nitrometer.

To ensure that the air within the flask is under atmospheric pressure, the two-way tap is turned so as to open communication between the flask and the measuring-tube, and the pressure-tube adjusted so that the mercury stands at the same level in both tubes. The tap is then turned so as to connect the reservoir *n* with the measuring-tube, and the air from the latter entirely expelled, and the tube filled with mercury by raising the pressure-tube. The tap is then closed and the pressure-tube slightly lowered. Communication with the flask is again established, and the contents of the little tube tipped out into the flask so as to bring about the desired reaction. As the gas is evolved, the pressure-tube is gradually lowered so as to avoid the creation of any unnecessary pressure in the apparatus. When the action is completed, the mercury is brought to the same level, and the apparatus allowed to stand for half an hour for the gas to assume the atmospheric temperature, when the volume is read off. The atmospheric temperature and pressure are noted, and the usual corrections made (see p. 387).

PART III.

SECTION I.

Estimation of Carbon, Hydrogen, Nitrogen, Chlorine, Sulphur, and Phosphorus in Organic Compounds.

I. Carbon and Hydrogen by Combustion.

Epitome of Process.—These two elements are estimated simultaneously by one and the same series of operations, whereby the organic compound is burnt, and the carbon and hydrogen oxidised to carbon dioxide and water respectively. The oxidation, or combustion, of the organic compound is accomplished by heating it in a *combustion-tube* with copper oxide, in a gentle stream of air or oxygen. The products of the combustion are thus expelled from the tube, and are made to pass first through a weighed calcium chloride tube, and then through weighed potash bulbs (or soda-lime tubes). The increase in weight of the calcium chloride tube is due to the water, one-ninth of which represents the hydrogen in the organic compound ; while the gain in weight suffered by the potash bulbs is caused by the absorbed carbon dioxide, three-elevenths of which is the weight of the carbon in the compound.

Fitting up the Apparatus. (1) *The Combustion-tube.*—A piece of combustion-tube, about 8 cms. longer than the combustion furnace (which itself will be 70 to 80 cms. long*), and about 15 mm. bore, is rounded at the edges by just fusing the ends in the blowpipe flame. The tube is then thoroughly cleaned inside. For this purpose one end is closed with a cork, and a few cubic centimetres of strong sulphuric acid poured in at the other end. This is made to flow over the whole interior surface by tipping and rotating the tube. The acid is then poured away, and the tube thoroughly rinsed out with water, the cork being removed and a stream of water run through the tube. The tube is allowed to drain, and finally dried by gently warming it and blowing air through it from the bellows.

* For rough measures, 2·5 cms. = 1 inch.

Into one end of the tube a roll of copper gauze, *c*, Fig. 89, is thrust to a distance of about 20 cms. This is made by rolling a strip of fine gauze, 2·5 cms. wide, into a cylinder or plug, which will fit moderately tightly into the tube, so as to retain its place. The tube is then filled up to within 12 cms. of the other end with granular copper oxide ; * and a second roll of copper gauze, *c'*, the same length as the other, is pushed into the tube so as to confine the copper oxide.

The substance under analysis is contained in a platinum or porcelain boat, *b*, which is pushed into the tube nearly close up to the copper-gauze roll.

Behind the boat is introduced a loose-fitting plug, *p*, the object of which is to concentrate the current of air or oxygen at this point, in order to prevent the backward diffusion of vapours or products of combustion of the substance in the boat. This plug may be either a short roll of copper gauze, having a little wire loop by means of which it can easily be withdrawn ; or, better, a short piece of hard glass tube (which will just pass freely into the combustion-tube), closed at one end, and narrowed, but left

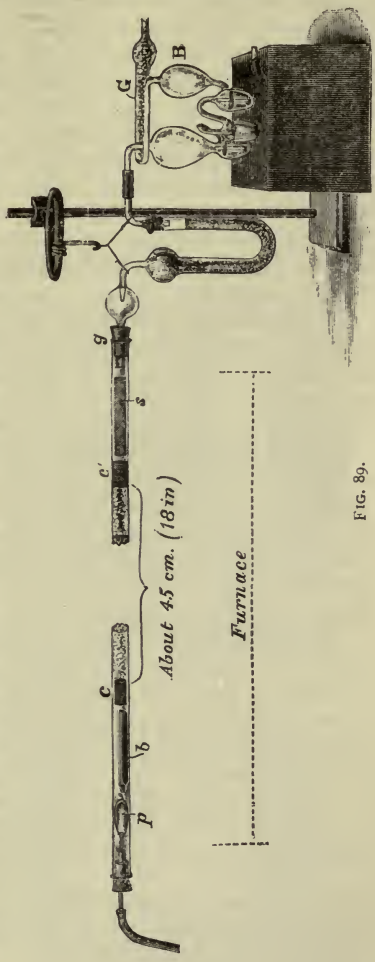

FIG. 89.

* Copper oxide made by heating the nitrate should not be used, as it is liable to evolve oxides of nitrogen when heated. Granular copper oxide is obtained by direct oxidation of the metal.

$NH_4NO_3 + HCl$

open, at the other end. This can readily be withdrawn by means of a piece of wire, bent into a small hook at the end.

The combustion-tube is closed at this end with a rubber stopper carrying a short piece of narrow glass tube, which projects about 3 mm. into the combustion-tube, the other end being connected to the apparatus for purifying and drying the air and oxygen. The space, S, at the other end of the tube is for the reception of a roll of either copper or silver gauze, about 6 cms. long, and sufficiently loose to admit of easy removal. If the organic compound to be analysed contains nitrogen, either the copper or silver roll will serve to decompose the nitrogen peroxide,* which, if allowed to pass from the tube undecomposed, would be absorbed by the potash, and thereby vitiate the carbon determination. When, however, the compound contains a halogen, the silver roll must be employed.

Before use, such a copper gauze roll should be first superficially oxidised, by heating for a few moments in a flame, and then heated in a stream of hydrogen. A number of rolls may be prepared at one operation, and may be kept bright by being corked in a tube.

(2) *The Combustion Furnace.*—When the combustion-tube is fitted up, it is laid in the furnace,† and should project about 3½ cms. at each end. A shallow trough or tray of sheet iron runs the entire length of the furnace, and in this a bed for the tube is made by first laying in the trough a strip of asbestos cloth, wide enough to project over the sides of the iron trough, so that the tube shall rest uniformly upon the asbestos without coming in contact with the iron.

(3) *The Calcium Chloride Tube.*—This is filled and prepared precisely as described on p. 203.‡ When not in use, the ends of the tube are closed by short rubber tubes plugged with pieces of glass rod. These caps are always removed while the tube is being weighed, but immediately replaced until the apparatus is required for the combustion.

The calcium chloride tube is attached to the combustion-tube by means of a rubber stopper, and is conveniently supported by a retort stand and ring, as shown in the figure.

* $4Cu + 2NO_2 = 4CuO + N_2$.

† Erlenmeyer's gas furnace, which consists practically of a row of Bunsen burners, is one of the best forms.

‡ As samples of calcium chloride are sometimes slightly alkaline, it is desirable, when the tube is freshly filled, to pass a stream of dry carbon dioxide through it for a few minutes, and then to displace the carbon dioxide by a current of dry air, which should be passed through the tube for about half an hour.

(4) *The Potash Bulbs.*—These may be either the ordinary Liebig's bulbs, or the more modern Geissler's apparatus, shown at B, Fig. 89. They are charged with a strong solution of caustic potash by dipping the tube projecting from the larger bulb into a small beaker or dish containing the potash, and sucking the liquid into the apparatus by means of a piece of rubber tube upon the opposite end. A little guard tube, G, filled with fragments of solid caustic potash, is attached to the bulbs in order to prevent the loss of water-vapour, which would otherwise result from the passage through the solution of the dry gases passing from the combustion-tube. Just as with the calcium chloride tube, when not in actual use the ends of the tubes are closed with rubber caps, which are removed while the apparatus is being weighed.

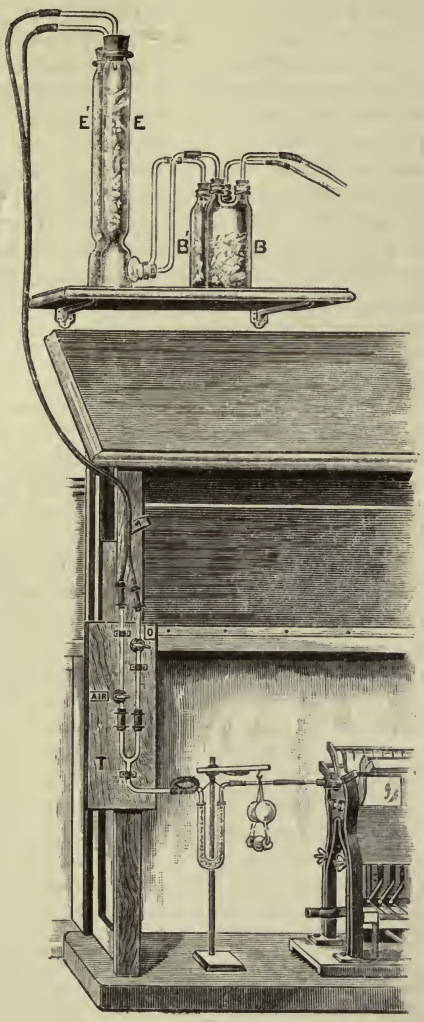

FIG. 90.

(5) *The Apparatus for Purifying the Air and Oxygen.*—This apparatus must be fitted up in duplicate, so that either air or oxygen can be admitted into the combustion-

tube in a purified condition without the loss of time which would result if one gas were made to follow the other through the whole apparatus. Fig. 90 shows a convenient arrangement for the purpose.

Each gas (contained in gas-holders, or compressed in cylinders) is passed first through a two-necked bottle, B, B′, nearly filled with pumice moistened with sulphuric acid. They then pass through the eprouvettes E, E′, which are filled with fragments of solid caustic potash. This part of the apparatus, when once charged, may remain undisturbed for several months, and may conveniently be placed upon a shelf out of the way. The gases may be conducted to it and led away from it by means of fine "compo" pipe 3 mm. in the bore, which may be carried down the wall to the side of the draught chamber, in which the combustion furnace is placed. At this point they are joined to two limbs of a bridle-tube, T, by means of short rubber connections, each with its screw-clamp or stop-cock; these joints should all be securely wired. The third limb of the bridle-tube is attached to a U-tube filled with soda-lime, and this in its turn is connected to a set of Liebig's bulbs containing strong sulphuric acid. By manipulating the taps, either oxygen or air can be admitted into these two tubes, and the rate at which the gas passes is seen by the bubbles travelling through the bulbs containing the sulphuric acid.

Testing the Apparatus.—When the apparatus is fitted up, it is necessary, before proceeding to make an actual combustion, to ensure the complete removal from the combustion-tube of every trace of moisture and of combustible matter. The calcium chloride tube and the potash bulbs are for this purpose removed, and the roll of copper gauze is introduced into the space S (Fig. 89).* The boat and the glass plug *p* are also removed.

The combustion-tube is then heated throughout its entire length to a low red heat for about 20 minutes, while a slow stream of the dried and purified air is passed through it. The air-supply should be then stopped, and the air contained in the oxygen purifying apparatus made to pass through the tube by sweeping it out with a stream of oxygen. This may be passed rather more rapidly than at first, so that in about 15 minutes oxygen will be issuing from the extreme end of the tube.

* It is advisable to place this roll in the tube at this stage, even although the combustions, which are to be first made, are of substances which do not contain nitrogen; so that afterwards, when the copper may be required, its freedom from organic matter will be assured. Moreover, in case the ordinary copper oxide (prepared from the nitrate) is the only preparation at hand, the presence of this copper roll will serve to decompose the oxides of nitrogen which are derived from this source.

While this is going on, the calcium chloride tube and the potash bulbs are weighed, the caps being removed for the short time occupied by the weighing.

The passage of the oxygen is then stopped, and the weighed tubes attached, the ends of the glass tubes of the two pieces which are connected by the rubber union, being pushed up within the rubber so as to touch each other.*

A slow stream of air is now passed through the apparatus, the rate being that which would be adopted during an actual combustion, namely, about two bubbles per second, as they pass through the bulbs. This is continued for about 15 minutes, after which the stream of air is replaced by a stream of oxygen at about the same rate for another 15 minutes. The potash bulbs and calcium chloride tube are then carefully disconnected, and their ends immediately closed with their caps. After a short interval, during which they are allowed to assume the ordinary temperature, they are weighed (as usual, without the caps), and if the operation has been successfully carried out, their weight should have undergone no increase. If, on the other hand, either piece of apparatus has gained more than 3 or 4 milligrams, it shows that the first part of the operation has not been complete, and that either moisture or carbon dioxide is still being evolved. In this case the passage of air through the still heated tube must be continued for a short time, and another "blank" experiment made by replacing the calcium chloride tube and potash bulbs, and allowing first air, and then oxygen, to pass through the entire apparatus for 15 minutes each. The absorption apparatus is then detached and reweighed, when, unless something is seriously wrong, the weights will be found to have undergone no change.

The apparatus is now in a condition to be used for a series of "combustions," and need not be further tested until it becomes necessary to replace the combustion-tube. If the asbestos bed has been properly arranged, so that the tube rests uniformly all along it, and if care is exercised in heating the tube, so as not to heat too

* It is of the greatest importance that the stopper or cork through which the calcium chloride tube passes should not become over-heated during a "combustion," and yet at the same time the tube must be sufficiently warm right up to the cork to prevent moisture from condensing before it passes into the bulb. If the combustion-tube projects 4 cms. beyond the furnace, as directed on p. 416, the cork is practically quite safe, but the additional precaution may be adopted of placing a small screen, cut out of asbestos cardboard, over the tube just outside the furnace. This screen, however, should be removed towards the end of the process to make sure that no moisture has deposited before passing into the absorption-tube.

suddenly at first, and not to raise the temperature unnecessarily high, whereby the glass is softened, a combustion-tube made of the best hard glass will stand being used over and over again for a great many analyses.

Typical Examples of Combustions.

(*a*) **Combustion of Non-volatile Solids.**—One of the most suitable substances to employ for a first experiment is cane sugar, as it is readily obtained in a state of purity, and the percentage of hydrogen it contains is comparatively high. The pure crystallised compound is finely powdered, and dried in a steam-oven.

A porcelain or platinum boat (previously proved to be of such a size that it will pass easily into the combustion-tube) is supported on a pipeclay triangle, and heated to low redness by means of a Bunsen flame ; if a porcelain boat is employed, it must be heated cautiously.

It is then placed to cool in the desiccator, and when cold, it is weighed. It must be handled as little as possible by the fingers, and not at all if the hands of the operator are at all moist.

From 0·2 to 0·3 gram of the dry sugar is weighed into the boat, which is then pushed into the combustion-tube, almost close up to the roll of copper gauze. The clean dry glass plug is next introduced, and the tube is then connected to the apparatus for supplying the stream of dry and pure air.

The weighed calcium chloride tube and potash bulbs are then attached, the projecting end of the combustion-tube being firmly held with one hand while the calcium chloride tube is being fitted on, so as not to disturb the boat and its contents.

The portion of the tube from S (Fig. 89) to the copper gauze roll *c*, that is, the part containing the whole of the copper oxide, is first heated to redness, after which a slow stream of air (not faster than two bubbles per second) is passed through. The heating is now gradually extended towards the boat by turning on one burner at a time—at first with a small flame, and then increasing it.

The success of the operation hinges upon this part of the process, therefore it must be carefully watched, lest the heat be applied too rapidly.

The combustion of sugar is usually completely effected with a stream of air, without the admission of pure oxygen ; but if any traces of a black residue are seen to persist in the boat towards the end of the operation, a stream of oxygen may be substituted for

the air for a few minutes, after which the oxygen is stopped, and the air again passed through for about 10 or 15 minutes.

In this way the whole of the water-vapour and carbon dioxide is swept out of the tube into the absorption apparatus; and the portions of copper oxide which during the combustion had become reduced are re-oxidised.

The potash bulbs and calcium chloride tube are then removed, their ends capped, and, after being allowed to assume the ordinary temperature, they are weighed.

$$\underset{18}{H_2O} : \underset{2}{H_2} = 9 : 1$$

$$\text{therefore } \frac{\text{weight of } H_2O}{9} = \text{weight of hydrogen}$$

$$\underset{44}{CO_2} : \underset{12}{C} = 11 : 3$$

$$\text{therefore } \frac{\text{weight of } CO_2 \times 3}{11} = \text{weight of carbon}$$

From the numbers thus obtained, the percentage of hydrogen and carbon are calculated. The oxygen is estimated by difference.*

The theoretical composition of sugar, calculated from the formula $C_{12}H_{22}O_{11}$, is hydrogen, 6·43; carbon, 42·10; oxygen, 51·47.

The experimental errors of a carbon and hydrogen determination are usually in the direction of a deficit of the former, and a slight excess of the latter, element. If, in the analysis of sugar, the carbon falls more than 0·3 below the theoretical value, or the hydrogen more than 0·1 above it, a duplicate experiment should be made.

(*b*) **Combustion of Volatile Solids.**—For practice in the combustion of a volatile solid, benzoic acid may be employed.

Benzoic acid, $C_6H_5.COOH$: carbon, 68·852 per cent.; hydrogen, 4·918 per cent.

From 0·4 to 0·5 gram of the compound is weighed out into the boat, but before the latter is introduced into the combustion-tube, the weighed calcium chloride tube and potash bulbs are attached, and the tube is heated to redness to within about 2½ cms. of the copper roll *c* (Fig. 89). The boat is then carefully pushed in, the glass plug quickly inserted, and connection made with the gas-drying apparatus. A slow stream of air is admitted, and then the heating *very gradually and cautiously* extended in the direction of

* In cases where the substance under analysis leaves an incombustible residue or ash, the boat is withdrawn after the tube has cooled, and placed in a desiccator until cold, when it is weighed. Deducting the weight of the boat gives the weight of the ash.

the boat. The more volatile the substance is, the more gradually must the heating be extended towards the boat containing it.

The remainder of the process is conducted as in the former example, the stream of air being replaced by pure oxygen towards the end of the operation.

(*c*) **Combustion of Liquid Compounds.**—If the liquid is not appreciably volatile at ordinary temperatures, and at the same time does not absorb atmospheric moisture, it may be weighed out into the boat and treated as in the above example.

Moderately volatile liquids are enclosed in small glass bulbs, made by drawing out a piece of narrow glass tube, as shown at A (Fig. 91), and then blowing the small tube into a bulb, B. The bulb must be of such a size that it will lie in the boat, and pass into the combustion-tube in this position.

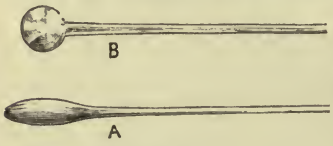

FIG. 91.

As an example, benzene, C_6H_6, may be employed. One of the little bulbs, with a capillary stem about 3 cms. long, is weighed. It is then gently warmed, and the stem dipped into the liquid in a small beaker. When about 0·25 gram has entered the bulb, the tip of the stem is sealed by bringing it into a small gas-flame. The bulb is then weighed.

As in the case of the volatile solid, the absorption apparatus is attached, and the combustion-tube is raised to a red heat to within about 4 cms. of the copper coil *c* (Fig. 89) before the boat containing the bulb is introduced.

A very slight scratch with a fine-cut file is made on the capillary stem of the bulb, near to the closed end,* and the bulb is laid in the boat in such a position that the fine point projects over the end of the boat beyond the file-mark. In this way the liquid is prevented from running up into the capillary tube. When all is in readiness, the end of the fine tube is broken off, the fragment is deposited in the boat (in order that any traces of liquid it contains may be included), and the latter immediately pushed into the combustion-tube, the stem of the bulb foremost. The plug is quickly introduced, and the tube connected with the gas-drying apparatus. The process is then continued as in the former example.

* The liquid should not be more in the capillary tube than can be avoided. It may be driven back into the bulb so as to have a clear place near the end where the stem is afterwards to be broken, by gently warming the tube with a very small flame.

Liquids which are highly volatile are vaporised *outside* the combustion-tube, and the vapour slowly passed over the heated copper oxide. For this purpose a piece of moderately narrow glass tube is drawn out into thick-walled capillaries in two places, so as to leave a piece of the original tube about 2½ cms. (1 inch) long. In order that the walls of the capillary tubes shall be thick, the glass tube is heated in the blowpipe over as long a surface as the flame will allow, until the walls of the tube have softened and thickened as much as possible without falling together. The tube is then *slowly* drawn out the desired length, about 8 cms. (3 inches). It is then bent in the manner shown in Fig. 92. The tube is first weighed, after which about 0·3 to 0·5 gram of the liquid is introduced, and the fine drawn-out ends sealed in a flame. The tube is then re-weighed. The liquid must not be allowed to get up into the horizontal capillary tube. A cork, previously selected to fit the combustion-tube, and dried in an air-oven, is fitted on to the horizontal limb of the little tube, and the apparatus is cooled by being immersed in ice-water, or in a freezing mixture (depending upon the volatility of the liquid), so as to reduce the tension of its vapour to an insignificant pressure. Thus, for such a liquid as ether, ice-water may be used.

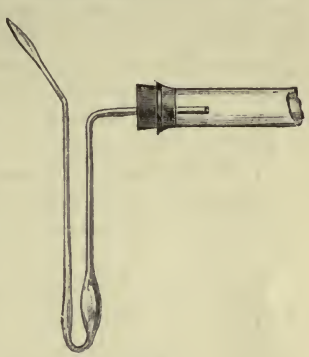

FIG. 92.

The weighed absorption apparatus having been attached, and the combustion-tube heated to redness, the extreme end of the capillary tube projecting through the cork is cut off, and the cork inserted. The glass plug is not introduced in this case.

The temperature of the little tube containing the liquid is then allowed gradually to rise. If it is in ice-water, this may be done by gently applying heat to the water by bringing a small flame under the beaker, while, if it is in a freezing mixture, the gradual addition of ordinary water will be sufficient to raise the temperature.

In this way the liquid is slowly vaporised, and the vapour caused to pass over the heated copper oxide. When the liquid has entirely volatilised, a fine scratch is made with a file close to the sealed end of the apparatus, and the rubber tube from the gas-purifying apparatus is slipped on. The end is then snapped off

inside the rubber, and a gentle stream of air (afterwards followed by oxygen if the organic compound is rich in carbon) is passed through the tube until the combustion is complete, and the products have been entirely expelled into the absorption apparatus.

II. **Estimation of Nitrogen in Organic Compounds.** Nitrogen in organic substances may be estimated either by burning the compound with copper oxide in a combustion-tube (very much as in a carbon and hydrogen determination already described), and collecting and measuring the nitrogen that is evolved; or it may be indirectly determined by converting it into ammonia, and estimating the ammonia by one of the processes described in former sections. The former process (Dumas) is applicable to all nitrogenous organic compounds, while the latter cannot be employed in the case of those substances in which the nitrogen is present in a "nitro" or "azo" group.

1. **Nitrogen by Dumas' Method.**

Epitome of Process.—The organic compound * is mixed with copper oxide in a combustion-tube closed at one end, containing at the closed end a quantity of pure sodium bicarbonate. (This furnishes a supply of carbon dioxide with which to sweep out first the air, and finally the products of the combustion, from the tube.) A roll of bright copper gauze is introduced at the open end, to prevent the escape of any nitrogen in the form of oxides of nitrogen. The tube is closed with a cork and delivery tube, and the nitrogen is collected in a measuring-tube over caustic potash, whereby the carbon dioxide is removed.

A piece of combustion-tube (cleaned in the manner described on p. 414) is drawn off and sealed at one end before the blowpipe. The tube should be about 76 cms. (30 inches †) long, or of such a length that it can be heated to the extreme end when in the furnace.

A quantity of pure dry sodium bicarbonate ‡ is introduced, so that when the closed end is gently tapped on the table, the salt shall occupy a space of about 20 cms. A layer of about 12 cms. of powdered copper oxide is introduced, the tube being conveniently supported by a clamp in a vertical position. About 0·5 gram of the organic substance is then carefully introduced into the tube (the

* A suitable compound to employ for practice in the process is urea, $CO(NH_2)_2$.

† For rough measures, 2·5 cms. = 1 inch.

‡ Sodium bicarbonate of commerce sometimes contains appreciable quantities of ammonia, when manufactured by the ammonia-soda process. If the sample to be used is of unknown origin, a "blank" experiment should first be made, in which sugar or some other pure organic compound containing no nitrogen is used instead of urea.

weighing-bottle containing the compound is first weighed, and after a suitable quantity has been transferred to the tube, the bottle is reweighed), and by means of a long stout clean wire, bent like a corkscrew at the end, this is thoroughly stirred into the copper oxide below, to a distance of about one-half the depth of the copper oxide. A little more copper oxide (about 2½ cms.) is added (without withdrawing the wire), and the top layers of the lower stratum are mixed upwards into this. Once more a similar quantity of copper oxide is added, and the corkscrew thoroughly freed from any traces of the organic substance by being twisted up through this.

The tube is then filled to within about 12 cms. of the top with granular copper oxide, and lastly, a tolerably tight-fitting roll of bright copper gauze, 7 cms. long, is introduced. The tube is then removed from the clamp, and, while held in a horizontal position by the thumb and forefinger of both hands, it is gently tapped upon the table. In this way the contents are made to settle down, so as to leave a narrow channel or air-space all along the top. The tube is then laid in the furnace.

A well-fitting cork with a bent delivery tube is inserted, and that portion of the tube containing the granular copper oxide is heated to dull redness.

As soon as the tube is visibly red hot, the most forward portions of the sodium carbonate are heated so as to sweep out the air from the tube by means of the carbon dioxide so generated. Not more than half the carbonate should be thus used at this stage.

As soon as the heating of the carbonate is commenced, the delivery tube is attached, by means of a rubber connection, to the lower branch tube of a Schiff's burette, as shown in Fig. 93. At the bottom of the burette there is previously introduced a small quantity of mercury, sufficient to reach about 12 mm. (½ inch) above the junction of the branch tube, and a strong solution of caustic potash (1 part of solid KHO in 2 parts of water) is poured into the movable reservoir R. The tap *t* is then opened, and the burette filled with potash solution by raising the reservoir, after which the tap is again closed, and the reservoir placed in about the position shown in the figure. So long as air is still being expelled from the combustion-tube, gas will collect in the burette; but as it becomes swept out by the carbon dioxide, the ascending bubbles get smaller and smaller, until at last they are practically entirely absorbed by the potash. When this point is reached, the air which has collected is expelled by again cautiously raising the reservoir

and opening the tap, and the heating of the combustion-tube extended first to the roll of copper gauze, and then gradually along the tube towards the mixture of copper oxide and the organic substance.

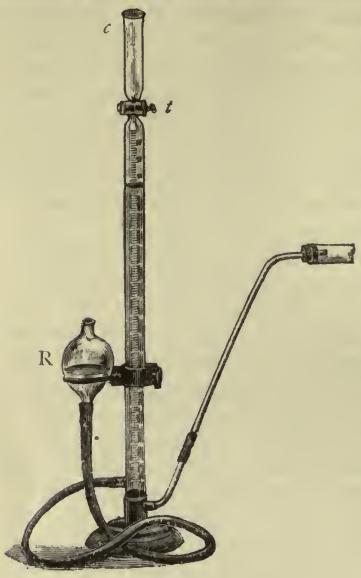

FIG. 93.

The nitrogen which is evolved, together with the carbon dioxide now filling the air-space of the tube, pass up into the burette, and, the carbon dioxide being absorbed by the potash, the nitrogen alone collects. When the evolution of nitrogen is completed, the remainder of the sodium bicarbonate is heated, whereby a fresh supply of carbon dioxide is generated, which drives out the remainder of the nitrogen now filling the tubes. This is continued until the bubbles, which enter the burette through the mercury, are absorbed as before by the potash.

In order to make sure that the carbon dioxide is completely removed, the cup *c* is filled up with fresh potash solution, which is slowly admitted into the burette by cautiously opening the tap. When the operation is completed, the delivery tube is withdrawn from the rubber connector, which is then closed with a pinch-cock.* The reservoir is raised until the surface of the liquid it contains is level with that in the burette, in which position the apparatus is left for about a quarter of an hour, to ensure the perfect absorption of any traces of carbon dioxide which may be present. The levels are then exactly adjusted, and the volume of the nitrogen read off upon the graduated tube.†

* In some forms of Schiff's burette, the branch tube is sufficiently wide to admit of its being closed with a small cork; but in this case it is less easy to secure an air-tight connection with the delivery tube.

† Where a Schiff's burette is not at hand, the gas may be collected in a graduated glass tube filled with strong potash solution, and inverted in a trough of mercury. The point at which the air in the combustion-tube has been all swept out by carbon dioxide, must in this case be ascertained by placing the

The atmospheric temperature and pressure are noted, and the volume of gas reduced to N.T.P. by the formula on p. 388. As the tension of aqueous vapour exerted by such a strong solution of potash as is here used is considerably less than that of water alone, it is usual to give to p (see p. 388) the value of *half* the tension of vapour of water, taken from the table in the Appendix.

Since 1 c.c. of nitrogen, under normal conditions, weighs 1·254 milligrams, the weight in milligrams of nitrogen contained in that quantity of the organic compound employed for the analysis, is obtained by multiplying the corrected volume (in cubic centimetres) by 1·254.

Thus, suppose the corrected volume of nitrogen = 50 c.c., then the *weight* of nitrogen would be $50 \times 1{\cdot}254 = 62{\cdot}70$ milligrams = 0·0627 gram.

2. **Nitrogen by the Soda-lime Process.**

This method is based upon the fact that many organic substances containing nitrogen (see p. 424), when strongly heated with soda-lime, give up their nitrogen in combination with hydrogen as ammonia. By estimating the ammonia so evolved, the weight of nitrogen can be determined.

Epitome of Process.—The organic compound is mixed with dry granular soda-lime in a combustion-tube closed at one end, and containing a short layer of dry oxalic acid at its closed end (in order to furnish a stream of hydrogen wherewith to sweep out the ammonia at the end of the process). The evolved ammonia is absorbed in dilute acid contained in a Will and Varrentrap's bulb-tube, which is attached to the combustion-tube by means of a cork. The ammonia may be estimated either *gravimetrically*, by precipitation as the double ammonium platinic chloride, in which case the gas is absorbed in dilute hydrochloric acid (1 vol. acid to 4 vols. water), and the estimation carried out as described on p. 251; or it may be determined *volumetrically* by absorbing it in an excess of standard sulphuric acid, and then titrating with standard sodium hydroxide. The latter process is the more rapid.

end of the delivery tube beneath a separate tube (a test-tube, for example) filled with potash and inverted in the same trough.

At the conclusion of the combustion, the measuring-tube containing the gas is withdrawn from the mercury trough (by slipping a small dish underneath it) and transferred to a tall cylinder of water. The mercury and the remaining potash flow out, and are replaced by water, and after the whole has assumed a uniform temperature, the tube is lowered into the water until the level of the liquid inside and outside are the same, when the volume is read off. The temperature of the water and the barometric pressure are noted. In correcting the volume to N.T.P., the full value of the pressure due to aqueous vapour must be taken (compare above).

Into a clean dry combustion-tube, from 40 to 45 cms. long, is introduced a quantity of oxalic acid (previously rendered anhydrous by being heated in a steam-oven), sufficient to occupy about 5 cms. Upon this is added about the same quantity of dry granular soda-lime, which has been recently heated moderately strongly in a porcelain dish.

A quantity of soda-lime (judged to be sufficient to occupy about 10 cms. of the tube) is powdered in a dry porcelain mortar, and by means of a small clean spatula a weighed quantity (from 0·3 to 0·5 gram) of the organic compound (urea may be used as an exercise) is thoroughly mixed with the soda-lime.* The mixture is then transferred to a sheet of clean writing-paper, and carefully poured into the tube by holding the paper in the palm of one hand and bending it into a gutter. The mortar is then rinsed out with a little more powdered soda-lime, which is similarly transferred to the tube. The tube will now be rather more than half full. Granular soda-lime is added until it reaches to about 5 cms. of the mouth, and a plug of asbestos (previously heated to redness) is inserted to keep the materials in position. The tube is then tapped lengthways upon the table (see p. 425), in order to create a free air-passage along the top of the materials, and it is then laid in the furnace.

A measured volume of normal sulphuric acid (15 or 20 c.c., depending upon the capacity of the bulbs (Fig. 94), which should contain about the volume of liquid represented) is introduced into the bulbs, which are then connected to the tube by a tight-fitting cork. The portion of the tube extending back from the asbestos plug, containing soda-lime only, is first heated to a low redness; after which the heating is gradually extended along until the whole of the mixture of soda-lime with the organic compound has become heated. As the heat approaches the end of the tube, a little care must be taken that the oxalic acid is not decomposed before its time. The column of pure soda-lime which separates the mixture should serve to

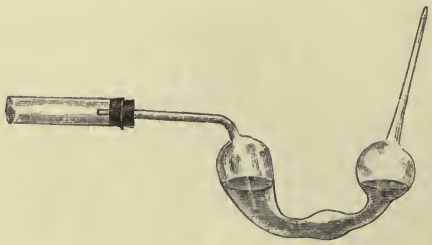

Fig. 94.

* Instead of mixing the materials in the mortar, the process may be carried out within the tube exactly as in the case of the former method (p. 425).

protect the acid, but the additional precaution may be taken of inserting in the furnace a small screen, made of asbestos cardboard, before beginning the operation.

As soon as the evolution of ammonia is complete, the heating is extended to the oxalic acid, which is decomposed in the presence of excess of alkali with evolution of hydrogen—

$$Na_2C_2O_4 + 2NaHO = 2Na_2CO_3 + H_2$$

In this way, the ammonia still filling the tube is driven out into the acid in the bulbs.* The bulbs are then disconnected and the contents transferred to a beaker, the bulbs being thoroughly rinsed out with water. The excess of sulphuric acid present is titrated with normal sodium hydroxide according to the method described on p. 327.

Each cubic centimetre of normal acid which has been neutralised by the ammonia, represents 0·0017 gram of ammonia, or 0·0014 gram of nitrogen.

3. **Nitrogen by Kjeldahl's Method.**—This process depends upon the fact that many nitrogenous organic compounds, when heated with strong sulphuric acid, have their nitrogen converted into ammonia, which at once unites with the acid, forming ammonium sulphate. From this salt the ammonia is afterwards expelled by means of caustic soda, and estimated by one of the usual methods.

Epitome of Process.—The nitrogenous compound is digested with strong sulphuric acid in a small round-bottom flask with a long neck, potassium sulphate being added towards the end of the operation in order to raise the boiling-point of the liquid. The mixture, after cooling, is diluted with water, and transferred to the apparatus (Fig. 53, p. 250), where it is treated with an excess of strong sodium hydroxide solution, and the ammonia determined by the volumetric method given on p. 327.

From 0·5 to 1·0 gram of the organic compound is weighed out

* In this process, and also in the Dumas' method previously described, the combustion may be conducted in a tube open at both ends (as described in the estimation of carbon and hydrogen, p. 415), and a stream of carbon dioxide or of hydrogen, as the case may be, passed through from a reservoir or generating apparatus outside. This modification of the processes, however, is not found to yield better results; and as in both cases the compound must be *mixed with* the contents of the tube, and cannot be introduced in a boat, the tube has to be dismounted and recharged for each combustion. In the carbon and hydrogen combustion, the open-tube method enables a series of determinations to be made in rapid succession without dismantling the apparatus, but in a nitrogen determination this is not the case, and it not only involves the use of unnecessary apparatus, but introduces manipulative difficulties in filling the combustion-tube.

into the digestion-flask, and 20 c.c. of strong sulphuric acid added to it.* The flask is then supported in an inclined position, and heated by means of a small flame nearly to the boiling-point until the mixture ceases to froth. The temperature is then raised, and the mixture (usually dark-coloured or black) boiled for about 15 minutes, carefully guarding against frothing. Ten to 12 grams of potassium sulphate are then added, and the mixture allowed to continue gently boiling until it is nearly colourless; after which the flame is removed, and the liquid allowed to cool. A little water is added, and the contents of the flask thoroughly rinsed out into the distilling apparatus shown on p. 250. It is there treated with caustic soda, and the ammonia distilled into an excess of standard sulphuric acid as described on p. 327.

III. Estimation of Chlorine† in Organic Compounds.

Epitome of Process (*Carius' method*).—A weighed quantity of the substance, contained in a thin tube or bulb, is introduced into a piece of stout combustion-tube, sealed at one end, along with a few crystals of silver nitrate and a quantity of strong nitric acid. The open end of the tube is then drawn out and sealed. The thin tube containing the compound is then broken, and the combustion-tube is placed in a hot-air bath, specially constructed for the purpose, and heated to a temperature necessary to ensure complete decomposition of the compound, for two or three hours. In this way the carbon and hydrogen are converted into carbon dioxide and water, while the liberated halogen combines with the silver, present as nitrate, and forms silver chloride. The tube is afterwards opened and the contents washed out, and the silver chloride filtered, dried, and weighed in the usual way.

A piece of combustion-tube about 60 cms. long, not too wide in the bore, and with tolerably thick walls, is sealed at one end before the blowpipe, care being taken not to allow the end to be *thinned* in the process. The organic compound is introduced into a thin glass tube, the end of which has been slightly enlarged before the blowpipe into a still thinner bulb (*a*, Fig. 95). This little bulb-tube is first weighed; about 0·3 to 0·5 gram of the substance is introduced, and the tube drawn off and sealed by means of a fine pointed blowpipe-flame at *a'*. The two portions *a* and *b* are then together weighed. The difference is the weight of the substance.

* As the sulphuric acid of commerce is liable to contain ammonium sulphate as an impurity, a blank experiment should be made with the sample of acid which is to be used; and the weight of nitrogen per cubic centimetre of the acid which is represented by this impurity, must be deducted from the result obtained in subsequent analyses.

† The process is equally applicable in the cases of bromine and iodine.

The portion *b* is left upon the scale-pan, while the bulb is carefully introduced into the combustion-tube, into which a few crystals (1 or 2 grams) of silver nitrate have previously been dropped. Fuming nitric acid (free from chlorine) is then added in quantity sufficient to occupy about 5 cms. of the tube. The tube is then held in an inclined position before the blowpipe, and drawn out into a thick capillary. This is done by heating the tube in the flame, revolving it slowly, until the softened walls thicken and almost fall together,

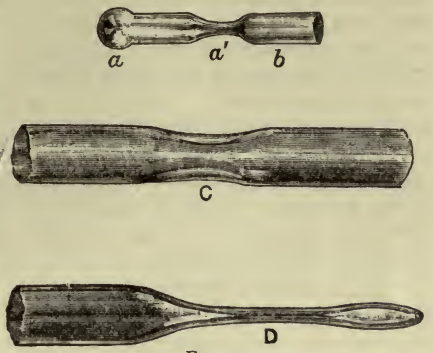

FIG. 95.

assuming the condition shown in C, Fig. 95. The glass is then gently pulled out, when the thick capillary shown at D will be obtained; the end is then sealed in the flame. When the tube has become quite cold, the little bulb within is broken by shaking the tube in such a way as to cause the bulb to strike against the walls, but without allowing any of the contents to get into the capillary end. The tube is then laid in the air-bath and gradually heated up to a temperature of 150° to 200°.

The air-bath consists of an oblong iron chamber or box, with a number of iron tubes closed at one end passing through lengthways; the tubes are screwed into the ends of the box, and fixed in a slightly inclined position, so that when the glass tubes are pushed in, the liquid contents will be kept at one end. The whole is supported on an iron stand, and heated by a row of small flames placed beneath. A thermometer, passing through a small hole in the top, registers the temperature. As great pressure is often developed in the glass tubes, it is desirable to place an iron screen or a brick opposite the end of the bath, so that, in the event of a tube bursting, the glass shall be prevented from flying about. After about two hours' heating, the gas is extinguished, and the glass tube allowed to become quite cold before being removed.

It must never be forgotten that the tube is now a somewhat dangerous object, and it must therefore be handled with caution. Such a tube should never be left lying about, as they sometimes

burst with great violence, without any apparent reason, even many hours after they have become cold.

It is carefully withdrawn from the bath, and immediately enveloped in a cloth, with the end of the capillary tube only projecting, and keeping it all the time in such a position that the liquid does not run up to the narrow end. Should any liquid have got into the end, it is carefully driven out by gently brushing a flame along that part of the tube.

The tube is then opened by cautiously introducing the tip of the capillary into a blowpipe-flame, so as to gradually soften the glass, which is then blown out by the outrushing gases from the tube.

On no account whatever must the tube be opened by scratching the capillary with a file and breaking off the point, as this is extremely likely to cause the tube to burst.

When the gas has escaped, the tube is cut at a point just below the narrowed portion by first making a scratch with a sharp file, and then touching the end of the scratch with the red-hot end of a piece of glass or wire. The contents of the tube are then transferred to a beaker, the tube and the cut-off piece being thoroughly rinsed into the beaker.

Besides the silver chloride, there will be the remains of the glass bulb-tube. As the latter will probably have been broken at the blown-out and thinner end, it is generally possible to pick out, with a platinum wire, the greater part of the glass in a single large piece. This is rinsed thoroughly, and carefully placed on a piece of filter-paper in a steam-oven to dry. It is then conveyed to the balance, and weighed along with the drawn-out end which has been left there. The difference between this weight and the original weight of the empty bulb-tube, will represent the weight of the fragments of glass still remaining admixed with the silver chloride, and which therefore must afterwards be deducted from the weight finally obtained.

To the acid liquid sufficient sodium hydroxide (free from chloride) is added to neutralise most of the acid, and the mixture is then filtered, every particle of the broken glass, as well as the silver chloride, being carefully brought on to the filter. The precipitate is washed, dried, and treated in the usual way.

From the weight of silver chloride (after deducting the weight of the fragments of glass) the percentage of chlorine in the compound is calculated.

IV. **Estimation of Sulphur and Phosphorus in Organic Compounds.**—The oxidation of the organic compound by means

of strong nitric acid in a sealed tube converts sulphur into sulphuric acid, and phosphorus into phosphoric acid. In either case, therefore, the process is carried out as in the estimation of chlorine, but without the silver nitrate.

In the case of sulphur, the contents of the tube are transferred to a dish, and the nitric acid expelled by evaporating the mixture nearly down to dryness. Dilute hydrochloric acid is added, and the sulphuric acid precipitated as barium sulphate in the usual way (p. 258). When phosphorus is being estimated, the acid liquid is neutralised with ammonia, and the phosphoric acid precipitated as ammonium magnesium phosphate (p. 264).

SECTION II.

Miscellaneous Physico-chemical Determinations.

Specific gravity of solids and liquids.
Boiling-point.
Melting-point.
Vapour density.

(1) Determination of the Specific Gravity of a Solid.*

(*a*) *Solid Substances which are not acted upon by Water.*

Principle.—When a body is weighed suspended in a liquid, its weight is *diminished* by the weight of the liquid displaced. Hence, therefore, if the body is weighed first in air, and again when immersed in water, the difference between the two weights is the weight of the water displaced by the body ; that is, the volume of water which is equal to the volume of the body.

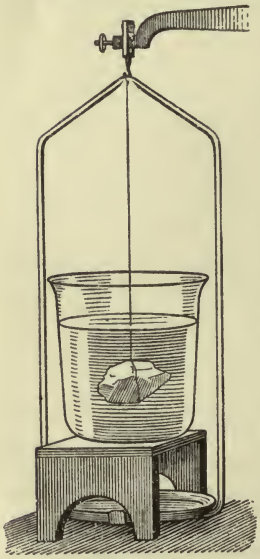

Fig. 96.

Example.—A fragment of quartz or flint or other mineral, about the size of a walnut, is weighed in the ordinary way. It is then suspended by means of a thread of silk, or a horsehair, from the beam of the balance, in such a manner

* The specific gravity of a solid or liquid substance is the ratio between the weight of a given volume of the substance and the weight of the same volume of water at its point of maximum density (taken as 4° C.). It is, therefore, obtained by dividing the former weight by the latter. As, however, it is more difficult to maintain a uniform temperature at 4 than at the common atmospheric temperature, the operations are usually conducted at 15·5.

that it will reach to about the middle of a small beaker supported upon a wooden bridge which stands over the pan, as in Fig. 96, leaving the latter free to move. The beaker is nearly filled with water at 15°·5, and any air-bubbles adhering to the solid substance are carefully removed by means of a feather or small camel's-hair brush.* In this position the substance is again weighed.†

If a = the weight in air, and b = weight in water—

then $a - b$ = the weight of water displaced

therefore $\frac{a}{a-b}$ = specific gravity of the substance.

(*b*) *Solid Substances which are acted upon by Water.*—When the solid is dissolved, or otherwise acted upon by water, some other liquid of *known specific gravity* is employed which exerts no action upon the body.

If x = density of the solid as compared with the liquid,

and y = specific gravity of the liquid—

then $\underset{\text{(sp. gr. water)}}{1} : y :: x$: specific gravity of solid compared with water.

EXAMPLE.—A crystal of copper sulphate (or alum, nitre, sodium thiosulphate, etc.) is first weighed in the usual manner. It is then suspended in a beaker containing benzene (C_6H_6, sp. gr. 0·885), and again weighed, care being taken, as in the former example, to remove all air-bubbles.

If a = weight in air, and b = weight in benzene—

then $\frac{a}{a-b}$ = density as compared with benzene = x

and $x \times y$ = specific gravity compared with water.

(*c*) *Powdered Substances.*—When the substance is in a powdered condition, the weight of water which it displaces is ascertained by weighing it in a small bottle which is filled up with water. The weight of the empty bottle is known, and the weight of water it contains when full is also known.

* A porous substance, like charcoal, for instance, must be first placed in water beneath an air-pump receiver and exhausted.

† If the substance is *lighter* than water, a weight is attached to it in order to sink it. The weight of this *sinker* when suspended in water is first ascertained. Then, if a = weight of substance in air,

b = weight of substance and sinker together in water,

c = weight of sinker in water—

then $\frac{a}{a-(b-c)}$ = specific gravity of the substance

If a = weight of powder in air,
b = weight of powder and water,
c = weight of water—

$$\text{then } \frac{a}{a-(b-c)} = \text{specific gravity of the powder}$$

A small bottle with a perforated glass stopper (known as a specific-gravity bottle) is exactly weighed in a perfectly clean and dry condition. It is then filled with water at 15°·5, and the stopper inserted. The small quantity of water which is thereby extruded through the bored stopper is wiped off with a clean cloth, and the bottle quickly weighed. (As sold, these bottles are marked with the weight of water they are supposed to hold at this temperature.) From this the weight of water it contains (c in the above formula) is ascertained once for all.

Into the dry bottle a quantity of the powder is placed, and the bottle weighed. From this the weight of powder in air (a) is found by deducting the known weight of the empty bottle. The bottle containing the powder is then filled with water at 15°·5, being gently tapped to disentangle any air-bubbles. The stopper is inserted, and after carefully wiping off the overflow the bottle is again weighed. By subtracting the weight of the empty bottle, this gives the weight of powder + water (b). From these data the specific gravity is calculated by the above formula.

(2) **Determination of the Specific Gravity of a Liquid.**—This may be ascertained by means of the specific-gravity bottle described above. It is filled with the liquid in question at a temperature of 15°·5 and weighed. Deducting the weight of the empty bottle gives the weight of the liquid. The weight of the same volume of water at the same temperature being already known, the specific gravity of the liquid is at once ascertained by dividing the former by the latter.

Instead of the specific-gravity bottle, a thin glass U-tube, drawn out at each end to a capillary, may be employed. The liquid is drawn into the tube by dipping one extremity into the bottle containing it, and applying a gentle suction to a piece of rubber tube attached to the other end. The liquid is then brought to the temperature of 15°·5 by immersing it in a beaker of water at this temperature, after which it is carefully wiped and weighed.

(3) **Determination of Boiling-point.**—The liquid is gently heated in a tubulated distilling-flask (a "Wurtz" flask) fitted with a cork, through which is inserted a thermometer, the bulb of the

latter being a little above the surface of the liquid. The flask may be connected to a condenser in order to recover the portion of the liquid which is vaporised during the process. A fragment of scrumpled platinum foil placed in the flask causes the liquid to boil more regularly.

The point at which the mercury in the thermometer remains constant is noted, and where only moderate exactness is required this temperature may be taken as the boiling-point.

In more exact determinations, either a correction must be made for the cooling of the mercury in such portions of the column as extend above the cork, or else the operation must be performed in such an apparatus as to ensure the equal heating of the entire thread of mercury.

In the former case a second thermometer is lashed to the first outside the flask, in such a manner that the bulb lies midway between the cork and the highest point to which the mercury reaches, so as to record the average temperature of that portion of the mercury thread which extends above the cork. The correction which is added to the observed temperature is then made by means of the following formula :—

$$n(t - t') \times 0{\cdot}000143$$

where n = number of degrees over which the mercury is not exposed to the heated vapour ;

t = observed temperature ;

t' = mean temperature of the outside mercury (given by the second thermometer) ; and

0·000143 = apparent coefficient of expansion of mercury in glass.

More exact determinations of boiling-points are made by means of the apparatus shown in Fig. 97. The vapour from the boiling liquid passes up the central tube, and then down through the annular space between the inner and outer tubes before it finally issues through the lateral branch tube. This side tube, which extends for a considerable length, is connected to a condenser.

In this apparatus, not only is the whole of the mercury thread of the thermometer exposed to the hot vapour, but the tube through which it passes is itself surrounded by a jacket of the same vapour. In this way cooling due to radiation is reduced to a minimum.*

* It will be obvious that when a boiling-point is to be determined with sufficient exactness to necessitate the use of this apparatus, a thermometer which has been standardised must be employed, and the instrument must be one having a sufficiently open scale to render it possible to read small fractions of degrees.

It must be remembered that the temperature at which a liquid boils is influenced by pressure ; thus when we say that the boiling-point of water is 100°, it is understood that the liquid boils at this temperature under normal atmospheric pressure. When making a boiling-point determination, therefore, the barometric pressure at the time must be noted. If this is greater or less than 760 mm., then either the observed boiling-point is recorded as having been taken under that particular pressure, or a correction for pressure must be introduced.

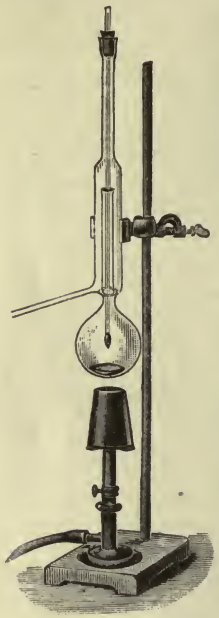

FIG. 97.

There is, however, no formula of general application by means of which this correction can be made, for the reason that the extent to which the boiling-point is influenced by variations of pressure is different with different liquids. If, therefore, the liquid under examination is an unknown substance, its *exact* normal boiling-point (*i.e.* its boiling-point at normal pressure) can only be ascertained by making the determination at that actual pressure.

The extent to which liquids differ from each other with respect to the effect of pressure upon their boiling-points is, however, very slight, so that an *approximate* correction may be introduced by regarding them as all behaving as water does.

For each millimetre pressure (in the neighbourhood of 760 mm.) the boiling-point of water varies 0·0375° ; or, in other words, the boiling-point is lowered 0·1° for a decrease of pressure amounting to 2·68 mm., and raised by the same faction by a similar increase of pressure.

(4) **Determination of Melting-point.**—Provided a substance melts without undergoing decomposition, the temperature at which it fuses when in a state of purity is constant, and is termed its melting-point. This is determined by introducing the solid substance into a thin glass tube drawn down to a capillary end which is sealed. This little tube is lashed to the bulb of a thermometer either by small rubber rings (cut from ordinary rubber tube) or by wire, depending upon the particular liquid to be employed in the bath in which it is to be heated. Thus if a bath

of strong sulphuric acid is used, platinum wire should be employed. Fig. 98 shows the tube attached to the thermometer. The thermometer is then supported in a clamp, and lowered into a tall narrow beaker containing a liquid which may be heated well above the melting-point of the substance, without boiling. A small flame is placed beneath the beaker, and the liquid is kept constantly mixed by means of a stirrer, consisting of a glass rod bent in the form of a ring at one end. This is moved up and down in the beaker, and the moment the solid substance melts, the temperature is read off.

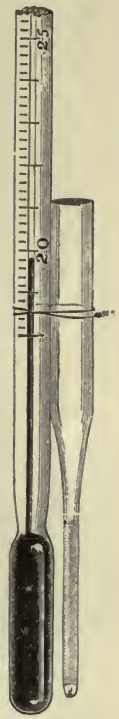

FIG. 98.

The thermometer is then raised out of the bath, which is allowed to cool somewhat, and the operation repeated. With some solids, such as fats, etc., the repetition of the determination must be made with a fresh specimen, as each time they are melted they undergo a slight decomposition or change which lowers the melting-point. If the substance is translucent, or is one in which from other causes it is difficult to observe the exact fusion point, the capillary tube may be open at the end, and the substance introduced by dipping the tube into a small quantity of the melted compound. The liquid rises by capillarity into the tube, which is then removed and the substance allowed to re-solidify. When the tube so charged is introduced as before into the bath, the moment the substance melts it is driven up the tube by the entrance of the liquid from the bath, and the temperature at which this movement is observed is noted. As in the boiling-point determination, the same correction must be made for the portion of the mercury thread which projects out of the bath.

(5) **Determination of Vapour Density.**—The density of a vapour is the ratio between the weight of a given volume of that vapour, and the weight of the same volume of another gas (under the same conditions of temperature and pressure) which is taken as the standard or unit. The standard usually adopted is *hydrogen;* therefore the vapour density of a substance is in reality the specific gravity of the vapour of that substance compared with hydrogen.

Vapour Density by Victor Meyer's Method.—Of the various methods which have been devised for determining vapour densities, that of Victor Meyer is the one most suitable for general

laboratory practice, where a very high degree of accuracy is not desired.* The apparatus consists of a bulb-tube, *b* (Fig. 99), with a long, rather narrow stem, upon which near the top there is a branch tube of narrow bore. This bulb-tube is placed in a wider tube, in which a suitable liquid may be boiled in order that the bulb-tube may be heated by the vapour. A weighed quantity of the liquid whose vapour density is to be taken is introduced into the hot bulb-tube, which is then immediately closed with a cork. The liquid in vaporising displaces a volume of air equal to the volume of the vapour, and the air so expelled is collected over water in the graduated tube, under the ordinary atmospheric conditions of temperature and pressure, which are noted. The volume in cubic centimetres so measured is reduced to N.T.P., and the corrected number of cubic centimetres when multiplied by 0·0000896 (the weight in grams of 1 c.c. of hydrogen) gives the *weight* of an equal volume of hydrogen.

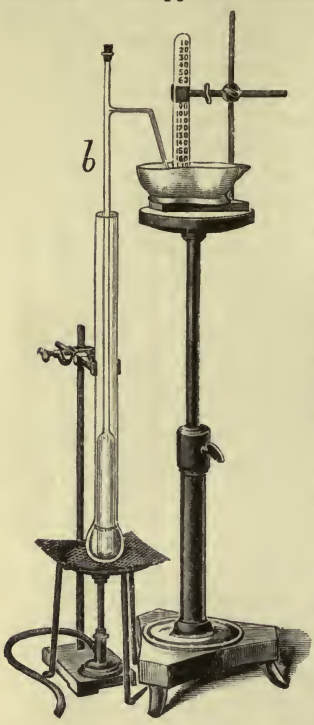

Fig. 99.

For practice the vapour density of carbon disulphide may be taken.† A little plug of glass wool or asbestos is pushed down to the bottom of the bulb-tube *b*, which is then placed in the outer tube, into which a small quantity of water has been introduced. The tube *b* must be perfectly dry inside. The top is closed with a good cork, and the water boiled. As the temperature rises and the air in *b* expands, the excess bubbles out through the water in the small trough. When the temperature is constant, and no more

* For descriptions of other methods, as Dumas', Hofmann's, etc., the student is referred to text-books on Physics.

† The specimen should be as pure as possible. It may be distilled, and that portion which passes over at 46° collected separately for the determination.

air is expelled, the graduated measuring-tube filled with water is brought over the end of the bent delivery tube. The apparatus is now ready for the introduction of the liquid.* This is contained in a tiny stoppered bottle, or in a fine glass tube sealed at one end and drawn to a capillary at the other (shown the actual size at *a* and *b*, Fig. 100). The bottle or tube is weighed first empty, and again when filled with the liquid (the tube is filled by gently heating in a flame, and then dipping the end into the liquid: and the capillary end is left unsealed). About 0·1 gram is a suitable weight of liquid to employ.

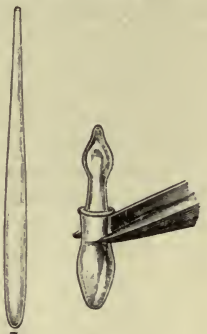

FIG. 100.

The cork is removed from the bulb-tube, and the little bottle (or tube), held in a pair of forceps, is dropped in, and the cork quickly replaced. If the bottle is used, the stopper is just loosened before dropping it in; if the tube is employed, it is dropped in capillary end downwards. The pad of glass wool or asbestos prevents the bulb from being fractured by the falling bottle. The liquid immediately vaporises and expels air from the apparatus, which collects in the graduated tube. When no more bubbles escape, the cork is removed.

The measuring-tube is then transferred to a large beaker filled with water at the temperature of the room, the transference being done by slipping a small porcelain dish under the tube as it stands in the water-trough. The tube is depressed in the water until the

* Other liquids than water are used in the outer tube or bath, when a higher temperature is required to vaporise the substance to be examined. It is only necessary that the temperature of this bath should be considerably higher than the boiling-point of the liquid to be vaporised, and that it should remain constant throughout the operation. It is not necessary to know what the actual temperature is. This fact often presents a difficulty to the young student, which is expressed by the constantly repeated question, "If the volume of gas or vapour is increased by rise of temperature, then surely the hotter the tube is, the greater the volume of vapour which will be produced when the liquid is introduced, and therefore a correspondingly greater volume of air will be displaced from the apparatus; how is it, therefore, that it is not necessary to take the temperature of the bath?" This difficulty vanishes when the fact is taken into account that, whatever is the temperature of the bath when the volatile liquid is introduced, the air within has *already been heated to that temperature*, and proportionately expanded or rarefied. Consequently at the higher temperature, although the volume occupied by the vapour is greater, and therefore the volume of air expelled is greater, it is only more *rarefied air*, which when cooled by collection over the water, is reduced to the same volume as the lesser bulk of less expanded air which would be displaced by the less expanded vapour at the lower temperature.

level of the liquid inside and outside is the same, when the volume is read off. The temperature of the water is taken, and height of the barometer is read.

The gas being saturated with aqueous vapour, the volume is reduced to N.T.P. by the formula given on p. 388.

The corrected volume so obtained is the number of cubic centimetres which the vapour of the carbon disulphide employed *would* occupy if it could exist under N.T.P.

Multiplying this by 0·0000896 gives the weight in grams of an equal volume of hydrogen at N.T.P.; and by dividing the weight of carbon disulphide employed by this weight of hydrogen, the vapour density of carbon disulphide is obtained.

6. **Determination of Molecular Weight by the "Freezing-point Method."**—When pure water is cooled under ordinary conditions, it freezes at 0° C.; but if the water be rendered impure by the presence of dissolved salts or other substances, it becomes necessary to cool it *below* 0° before ice begins to form. Thus, water containing 1 per cent. of sodium chloride in solution will require to be cooled to −0·6° before it begins to freeze. It is a familiar fact that a lower degree of cold is necessary to freeze sea-water than fresh.

When such aqueous solutions are cooled, the solid which begins to separate out is *pure ice*, and not the substance which is in solution in the water, provided the solution is sufficiently dilute.

What is true of water in this respect is true also of other liquids which are capable of being solidified. Thus, the freezing-point of pure benzene is 6°, but if a small quantity of benzoic acid (a solid) or aniline (a liquid) be dissolved in the benzene, then it will be found that this solution will require to be cooled *below* 6° before the benzene begins to freeze; and, just as in the case of water, it is the *solvent alone* which freezes out of the solution.

The discovery that a quantitative relation existed between the lowering of the freezing-point of a liquid and the amount of dissolved substance present was made by Blagden as long ago as 1788, who formulated the law that the depression of the freezing-point of aqueous solutions of the same substance was proportional to the amount of substance dissolved.

It was not, however, until the year 1871 that the important observation was made by Coppet that, in the case of certain chemically allied substances, if quantities which were *proportional to the molecular weights* were dissolved in equal volumes of the same solvent, the freezing-point was depressed to the same extent; or,

in other words, the solutions would have the same solidifying-point.

Upon these fundamental principles is based the process developed by Raoult, and known as Raoult's method (or the *cryoscopic* method) for determining molecular weights.

The extent to which the freezing-point of a liquid would be depressed by dissolving in 100 grams of it a *gramme-molecule* (*i.e.* a weight in grams equal to the molecular weight) of any substance, is spoken of as the *molecular lowering*, or *molecular depression*, of the freezing-point of that liquid ; and with certain qualifications, this is found, for one and the same solvent, to approximate to a constant.* Thus when water is the solvent, the molecular lowering of the freezing-point is about 18·5. For acetic acid the constant is about 39, while for benzene the value is about 49.

For example, a gramme-molecule of acetamide dissolved in 100 grams of water would depress the freezing-point 17·8°, while the same weight dissolved in 100 grams of acetic acid lowers the freezing-point of this solvent 36·1°.

This *molecular lowering* is calculated from experiments made with more dilute solutions in the following manner. Suppose a solution of cane-sugar ($C_{12}H_{22}O_{11}$, mol. wt. = 342) in water, containing 2·5 grams in 100 grams of water, is found by experiment to freeze at −0·137°. Then—

$$2{\cdot}5 : 342 :: 0{\cdot}137 = 18{\cdot}7 = \text{molecular depression}$$

$$\text{or, molecular depression} = \frac{ml}{g}$$

* This does not hold true in the case of substances whose molecules either dissociate or undergo some molecular aggregation in the particular solvent. Thus, in the case of water as solvent, it is found that such things as strong acids and bases and their salts—*electrolytes*, in other words—produce a molecular depression much greater than 18·5. This will be seen from the following table (Raoult) :—

Non-electrolytes.	Mol. depression.	Electrolytes.	Mol. depression.
Glycerol	... 18·5	Sulphuric acid ...	... 38·2
Mannite	... 18·1	Hydrochloric acid	... 39·1
Sugar	... 18·6	Nitric acid	... 35·8
Ethyl alcohol ...	... 16·6	Sodium hydroxide	... 36·3
Pyrogallol	... 18·0	Sodium chloride ...	... 35·1
Acetamide	... 17·7	Potassium chloride	... 33·8

In the case of non-electrolytes the phenomenon is concerned only with the molecules of the substance dissolved in water, while with electrolytes a certain proportion of the molecules (depending upon the degree of concentration) are believed to be dissociated into their ions.

where m = molecular weight of the dissolved substance,
l = observed depression of the freezing-point of the solvent, and
g = grams of substance in 100 grams of the solvent.

Having once established the constant representing the molecular lowering of freezing-point for any particular solvent, we are then in possession of all the data for determining the molecular weight of a substance which will dissolve in that liquid; for, substituting C for the constant in the above formula, we get—

$$m = \frac{Cg}{l}$$

The determination may be made by means of the apparatus shown in Fig. 101. This consists of a delicate thermometer graduated into $\frac{1}{100}^{\text{ths}}$ of degrees, which is fitted by means of a cork into the mouth of a large test-tube, A. The same cork also carries a short piece of narrow glass tube, C, through which the wire stirrer passes. The tube A fits into a wider tube (a boiling-tube), B, by means of a cork or a short piece of wide rubber tube. The whole is supported by a clamp and retort stand, and can be lowered into or raised out of the beaker or glass jar, F, containing the freezing mixture.*

As a convenient exercise in the use of the apparatus, the molecular weight of sugar may be determined by the lowering of the freezing-point of water.†

Adjusting the Thermometer.—The thermometer employed differs from ordinary thermometers, in that it has an adjustable zero. The scale covers a range of usually about 7 or 8 degrees, and in the most recent forms the zero is at the upper end of the scale. The total quantity of mercury in the thermometer is usually greater than is required to bring the column to zero when the bulb is placed in ice; hence it is necessary to so get rid of some of the mercury that the freezing-point of the solvent to be employed (in the present example, water) shall fall somewhere near the top of the scale—not necessarily exactly at zero, but conveniently near it.

* The Beckmann apparatus usually figured in instrument makers' price lists, contains a number of unnecessary appendages which give it an appearance of complication, and considerably add to its cost. It is only *necessary* to purchase the thermometer; for the rest, two boiling-tubes and a beaker or glass jar are all that is required.

† When the solvent employed is hygroscopic (glacial acetic acid, for example), the glass tube *c*, through which the stirrer passes, should be replaced by a ⊦ tube; and a slow stream of air, dried by means of calcium chloride or sulphuric acid, allowed to pass in through the side branch and escape at the top. In this way the air which is introduced by the movement of the stirrer is dry air.

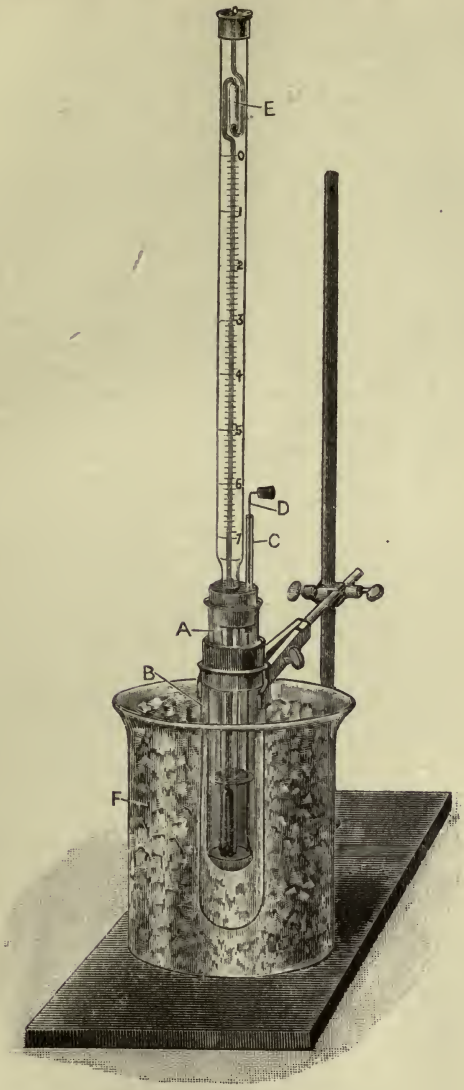

FIG. 101.

To accomplish this, the bulb is placed in water 3 or 4 degrees warmer than the freezing-point of the solvent, that is to say, about +3°, since water is to be the solvent.* The effect of this is to send the mercury up until it begins to enter the wider part of the bent stem E. By gently tapping the side of the instrument with the finger-tips, a small piece of the mercury becomes detached, and falls to the bottom of E, so that when the bulb is then placed in ice, the top of the column of mercury will come to rest upon the scale somewhere near the top graduations.

Into the tube A, perfectly clean and dry, a weighed quantity of water (about 20 to 25 grams) is introduced—either by weighing the tube, first empty, and then with the water, or by weighing the liquid out from a small flask. When the cork carrying the thermometer and stirrer is inserted, the bulb should be entirely immersed in the water. Tube A is then placed inside tube B, and the whole system lowered into a freezing mixture of ice and salt in the jar F. The object of the outer tube B is to render the cooling more gradual and uniform than would be the case if it were directly dipped into the freezing mixture.† As the water cools, it should be kept gently moving by means of the stirrer, the handle of which should be thrust into a small cork to prevent the warmth of the hand from being conducted to the liquid. The temperature will fall considerably below the freezing-point before solidification actually sets in, but the moment the supercooled liquid begins to freeze, the mercury in the thermometer will run up, and finally come to rest. This point, which may be conveniently read by means of a lens, is taken as the freezing-point of the water. The observation should be repeated two or three times, by removing tube A, and gently warming it with the hand until the ice is remelted, and then going through the freezing process again.

When the exact freezing-point of the solvent is established, a weighed quantity of pure cane-sugar is introduced by lifting the cork with the thermometer, and tipping the powdered substance out of a weighing-bottle.‡ When the substance has completely

* If benzene (M.P. 6°) were to be used as the solvent, then about 3° above *its* freezing-point; while if acetic acid (M.P. 16·5°), then a temperature of about 20° would be suitable.

† It is sometimes convenient, and a saving of time, to cool the water in A down to the freezing-point by first dipping the tube *direct* into the freezing mixture. Then removing it, wiping it dry, and, when the contents have again entirely remelted, placing it inside tube B, and then lowering the whole into the mixture.

‡ In the form of apparatus usually figured, tube A has a branch tube blown into it near the top, which is intended for the introduction of the substance;

dissolved (the process being aided by means of the stirrer), the system is lowered into the freezing mixture, and the freezing-point of the solution determined as before, by two or three repetitions of the operation.

For example :—

Weight of water taken	20·115 grams
Freezing-point indicated by thermometer	− 1·115°
Weight of sugar introduced	1·020 gram
Freezing-point of solution	− 1·395°

$$\text{Percentage strength of solution} = \frac{20{\cdot}115 \times 100}{1{\cdot}020} = 5{\cdot}07 = g$$

$$\text{lowering of freezing-point} = 1{\cdot}395 - 1{\cdot}115 = 0{\cdot}28 = l$$

$$\text{molecular lowering for water} = 18{\cdot}5 = c$$

$$\text{therefore molecular weight} = \frac{18{\cdot}5 \times 5{\cdot}07}{0{\cdot}28} = \mathbf{334{\cdot}9}$$

When a supercooled solution begins to freeze, and the temperature runs up to a point at which the thermometer remains for a time practically stationary, it will be seen that a certain quantity of the solvent has crystallised out. With the same solution, the amount which so separates depends upon the extent to which it was previously supercooled. This separation of a portion of the solvent obviously renders the remaining liquid a little more concentrated than the original solution, and from this it follows (1) that the observed temperature is slightly *lower* than the true freezing-point of a solution having the original strength; and (2) that, unless the extent to which the liquid is supercooled is the same each time the operation is repeated, the results obtained will not exactly agree. To obviate this, it is necessary to make a correction for the amount of solvent which thus separates.

Let t = number of degrees to which the solution is supercooled,
S = specific heat of the solution,
L = latent heat of the solvent,
M = mass of the solution, and
m = mass of solvent which separates out;

$$\text{Then } S \times t \times M = Lm$$

$$\text{and therefore } \frac{m}{M}(\text{the fraction which separates}) = \frac{St}{L}$$

For practical purposes, the specific heat of the solution may be taken as the same as that of the solvent; that is to say, the specific heat of the small quantity of the dissolved substance may be neglected. Therefore, in the case of water, S = 1 and L = 80; hence $\frac{St}{L}$ becomes $\frac{t}{80}$. That is to say, for each degree Centigrade to which the solution is supercooled, $\frac{1}{80}$ of the solvent separates out when the freezing-point is indicated, and the solution thereby becomes more concentrated to the same extent. And since the depression of the freezing-point is proportional to the concentration, the observed depression will be too low by the same fraction.

---

but, as a matter of fact, the substance is more conveniently introduced at the top as here described, and with the greater certainty that the whole of it actually falls into the liquid.

Applying this correction in the example given above—

The lowest temperature to which the mercury sank = −2·695
observed freezing-point = −1·395

therefore degrees of supercooling = 1·3

Hence $\frac{S/}{L}$ becomes $\frac{1{\cdot}3}{80} = 0{\cdot}01625$

therefore $0{\cdot}28 \times 0{\cdot}01625 = {\cdot}00455$
and $0{\cdot}28 - {\cdot}00455 = 0{\cdot}27545$ = corrected depression

Substituting this new value for l in the first calculation gives—

$$\frac{18{\cdot}5 \times 5{\cdot}07}{0{\cdot}27545} = 341{\cdot}3 = \text{corrected molecular weight.}$$

7. **Determination of Molecular Weight by the "Boiling-point Method."**—Just as the freezing-point of a liquid is *lowered* by the presence of dissolved substances, so the boiling-point is *raised* from the same cause, provided the substance is either non-volatile or exerts no appreciable vapour-pressure at the boiling-point of the solution.

The elevation of the boiling-point of a liquid caused by the solution in 100 grams of it of a gramme-molecule of such a substance is termed the *molecular elevation*, or the *molecular rise* of the boiling-point; and (with the same reservations as to substances which dissociate, as applied in the freezing-point method) for one and the same liquid this value is practically a constant.

In the following table are given the boiling-points and the molecular rise of boiling-point of a few common solvents:—

	Boiling-point.	Mol. rise of boiling-point.
Water	... 100·0° ...	... 5·2°
Benzene	... 80·5° ...	... 27·0°
Chloroform	... 61·2° ...	... 36·6°
Carbon disulphide ...	... 46·2° ...	... 23·7°
Ether	... 34·9° ...	... 21·1°

The operation may be carried out by means of the "Beckmann" apparatus, shown in a dissected condition in Fig. 102.

A weighed quantity of the solvent is introduced into tube A—in the case of very volatile liquids, such as ether, by weighing the tube with the ether, the tube being closed by corks. This tube is similar to tube A in the freezing-point apparatus, except that here the branch tube is necessary in order to attach a small reflux condenser, C_1, to return the liquid which would otherwise escape as vapour during the boiling. Small glass beads, *b*, are placed in the tube to a depth of about 20 mm. (a short inch), and the quantity of liquid employed must be such that the bulb of the thermometer is

well covered when the bottom of it nearly touches the beads. Sometimes a short piece of platinum is fused through the bottom of tube A, as seen at *p*, with a view to aid in the heating.

The thermometer is similar to that employed in a freezing-point determination, and must be previously adjusted, so that the boiling-

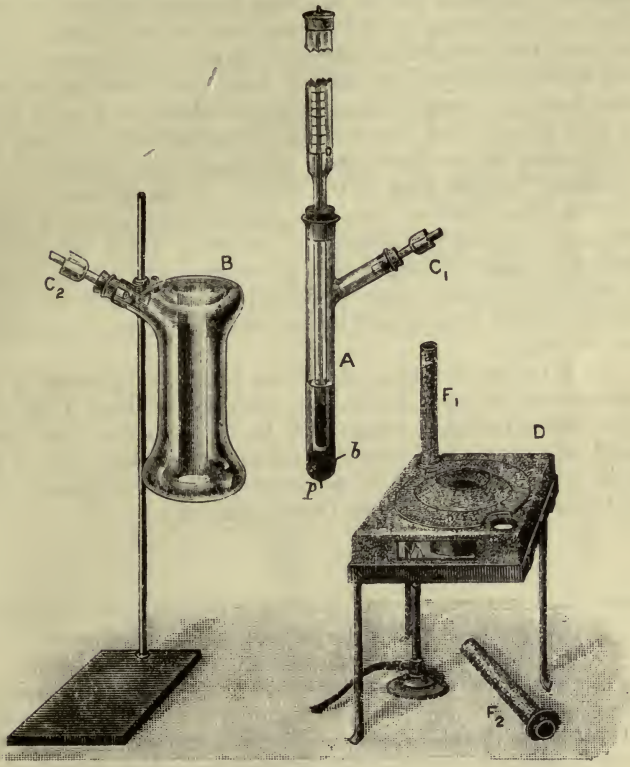

FIG. 102.

point of the liquid to be used may be indicated upon the *lower* parts of the graduated scale. The zero in this case is at the bottom of the scale.

Tube A is then placed within the jacket-tube B, which is open at both ends, but having a "jacket" blown upon it, in which can be boiled a small quantity of the same liquid as is in tube A.

This jacket is also connected to a reflux condenser, in order to return the vaporised liquid. The object of this tube is to surround tube A with an envelope which shall have a temperature as nearly as possible the same as that within A itself.

The apparatus is heated upon the asbestos support D. This somewhat resembles the lid of a box, provided with two asbestos chimneys for carrying away the waste heat from the lamps. From the centre hole, over which tube B is placed, there depends a short wide asbestos tube, and the lamp (or lamps) are placed so that their small flames are outside this tube, and therefore not directly below the glass tubes. The heat must be so regulated that a steady and brisk boiling of the liquid shall take place; any irregularity or "bumping" is quite fatal to the success of the operation. It is desirable to still further shield the apparatus by a screen of asbestos paper. When the mercury is stationary (after one or two gentle taps upon the stem of the thermometer with the finger-tips), the reading is taken—using a pocket-lens—after which the apparatus is allowed to cool, and the operation repeated, if necessary, once or twice.

When the exact boiling-point of the liquid, as registered by the thermometer, has been ascertained, a weighed quantity of the substance whose molecular weight is to be determined is then introduced, and after it has entirely dissolved, the boiling-point of the liquid is again taken. The molecular weight is calculated from the formula (similar to that for freezing-points)—

$$m = \frac{Cg}{R}$$

where C = constant (or mol. elevation of boiling-point of solvent),
g = grams of substance in 100 grams of solvent, and
R = observed rise of boiling-point.

The method is less capable of yielding accurate results than the freezing-point method, partly owing to conditions of experiment, and partly to variations of atmospheric pressure; but since the object is usually merely to decide between two values, one of which is a multiple of the other, a considerable experimental error is not of serious consequence.

As an exercise for practice in the method, the molecular weight of turpentine ($C_{10}H_{16}$ = 136) may be determined, using ether as the solvent.*

* Water is unfortunately not a convenient solvent, partly owing to dissociation suffered by so many substances in solution in this liquid, and partly on

EXAMPLE :—

Weight of ether taken	18·45 grams
Boiling-point indicated by the thermometer ...	3·25°
By means of a bent pipette, a weighed quantity of turpentine was introduced at the branch tube	0·8650 gm.
Boiling-point of the solution	3·94°

$$\text{Percentage strength of solution} = \frac{0{\cdot}8650 \times 100}{18{\cdot}45} = 4{\cdot}688 = g$$

$$\text{rise of boiling-point} = 3{\cdot}94 - 3{\cdot}35 = 0{\cdot}69 = R$$

$$\text{mol. rise of boiling-point for ether} = 21{\cdot}1 = C$$

$$\text{Hence mol. wt. of turpentine} = \frac{21{\cdot}1 \times 4{\cdot}688}{0{\cdot}69} = \mathbf{143{\cdot}3}$$

account of its very low molecular elevation of boiling-point. A volatile liquid like ether, on the other hand, necessitates very careful condensation. The most effective condensers are Cribb's double-surface condensers ; and the water with which they are supplied should be cooled by being passed through a few turns of "compo" pipe placed in a bowl of ice. The temperature of the water issuing from the condenser may thus easily be maintained at 5° or 6° C.

APPENDIX

TABLE OF ATOMIC WEIGHTS

1	2	Atomic weights. 3	4	1	2	Atomic weights. 3	4
Name.	Atomic symbols.	Approximate values.	More exact values.	Name.	Atomic symbols.	Approximate values.	More exact values.
Aluminium ...	Al	27	27·04	*Molybdenum* ...	Mo	96	95·9
Antimony ...	Sb	120	119·6	Nickel	Ni	59	58·6
Arsenic	As	75	74·9	*Niobium* ...	Nb	93·7	—
Barium	Ba	137	136·86	Nitrogen ..	N	14	14·01
Beryllium ...	Be	9	9·08	*Osmium* ...	Os	191	—
Bismuth	Bi	207·5	—	Oxygen	O	16	15·96
Boron	B	11	10·9	Palladium ...	Pd	106	106·2
Bromine	Br	80	79·76	Phosphorus ...	P	31	30·96
Cadmium ...	Cd	112	111·7	Platinum ...	Pt	195	194·3
Cæsium	Cs	133	132·7	Potassium (*kalium*) ...	K	39	39·03
Calcium	Ca	40	39·91				
Carbon	C	12	11·97	*Rhodium* ...	Rh	104	104·1
Cerium	Ce	141·2	—	*Rubidium* ...	Rb	85	85·2
Chlorine	Cl	35·5	35·37	*Ruthenium* ...	Ru	103·5	—
Chromium ...	Cr	52	52·45	*Samarium* ...	Sm	150	—
Cobalt	Co	59	58·6	*Scandium* ...	Sc	44	43·97
Copper (*cuprum*)	Cu	63	63·18	Selenium ...	Se	79	78·87
Didymium ...	Di	145	—	Silicon	Si	28	28·3
Erbium	Er	166	—	Silver	Ag	108	107·66
Fluorine	F	19	19·06	Sodium	Na	23	22·995
Gallium	Ga	70	69·86	Strontium ...	Sr	87·3	—
Germanium ...	Ge	72	—	Sulphur ...	S	32	31·98
Gold (*aurum*) ...	Au	197	196·8	*Tantalum* ...	Ta	182	—
Hydrogen ...	H	1	—	Tellurium ...	Te	125	—
Indium	In	113	113·4	Thallium ...	Tl	203·7	—
Iodine	I	127	126·54	*Thorium* ..	Th	232	—
Iridium	Ir	192·5	—	Tin	Sn	118	117·35
Iron (*ferrum*) ...	Fe	56	55·88	*Titanium* ...	Ti	48	—
Lanthanum ...	La	138·5	—	*Tungsten* ..	W	184	—
Lead (*plumbum*)	Pb	207	206·39	*Uranium* ...	U	239·8	—
Lithium	Li	7	7·01	*Vanadium* ...	V	51·1	—
Magnesium ...	Mg	24	23·94	*Ytterbium* ...	Yb	173	—
Manganese ...	Mn	55	54·8	*Yttrium* ...	Y	89·6	—
Mercury (*hydrargyrum*)	Hg	200	199·8	Zinc	Zn	65	64·88
				Zirconium ...	Zr	90·4	—

Reagents.

It is important that the reagents used in qualitative analysis should be made up of known definite strength, and that the strength should be indicated upon the bottles.* It is a great additional advantage, also, that the reagents should, as far as possible, have either a *uniform* strength (that is to say, equal volumes should possess equal chemical values, or be chemically equivalent), or, when this is not possible or desirable, the strength should bear some simple ratio to the equivalent strength.

By this is not meant that the reagents are to be prepared with an exactness in any way comparable to that required in making up the standard solutions used in volumetric analysis. For qualitative analysis, it is enough that the reagents bear a rough approximation to the exact strength indicated.

Unless some of the reagents were to be inconveniently dilute, it would not be possible to have them *all* chemically equivalent, owing to differences of solubility. For example, a solution of oxalic acid, which is *saturated* at 10°, is only equivalent to sulphuric acid consisting of 1 volume of strong acid in about 18 volumes of water.

In volumetric analysis, standard solutions are designated *normal solutions* when they are of such a strength that 1 litre contains a weight of the reagent in grams, equal to the *chemical equivalent* of that reagent. Thus, normal sulphuric acid contains 49 grams of H_2SO_4 per litre; normal hydrochloric acid 36·5 grams of HCl per litre, and so on (see p. 313). The *signature* employed to denote these normal or equivalent solutions is the letter N.

For qualitative analysis a convenient strength for the common acids and alkalies and general reagents is *five times this normal strength*. These are distinguished by the signature 5N.

A large number of other reagents, such as are used for special tests, are conveniently prepared of *normal strength*, and should bear the signature N; while others, which for special reasons (such as slight solubility, *e.g. calcium sulphate;* or the delicacy of their reactions, *e.g. ammonium thiocyanate*) should be more dilute, are prepared of suitable strengths, given in the following list of reagents, and the signature of the strength in all cases should be indicated upon the labels.

Thus, in the case of calcium sulphate, a *saturated* solution is employed; this contains one-thirtieth of the quantity of calcium sulphate required to produce a *normal* or *equivalent* solution, and its strength is denoted by $\frac{N}{30}$.

* It is greatly to be regretted that in many laboratories the practice still exists of providing the student with reagents concerning whose strength he is left absolutely in the dark. The effect of this upon the analytical work is only too familiar to those who have had much practical experience in teaching.

Again, ammonium thiocyanate being so delicate a reagent for the detection of ferric salts, a solution of one-fifth of the equivalent strength is conveniently strong. This is indicated upon the label by the signature $\frac{N}{5}$*.

Reagents of Five Times Normal Strength. Signature, 5N.

Sulphuric acid, H_2SO_4. Equivalent = 49. Ordinary concentrated acid, sp. gr. 1·84, has a strength 36 times normal, and may be designated 36N. One volume of strong acid diluted with 6 volumes of water = 5N.

Nitric acid, HNO_3.† Equivalent = 63. Concentrated acid, sp. gr. 1·42 = 16N. Five volumes of strong acid diluted with 11 volumes of water = 5N.

Hydrochloric acid, HCl.† Equivalent = 36·5. Concentrated acid, sp. gr. 1·16 = 10N. One volume of strong acid diluted with 1 volume of water = 5N.

Acetic acid, $C_2H_4O_2$. Equivalent = 60. Glacial acid, M.P. 10° C., = 17N. One volume of glacial acid diluted with 2½ volumes of water = 5N.

Potassium hydroxide, KHO. Equivalent = 56.

280 grams dissolved in water and diluted to one litre = 5N.

Sodium hydroxide, NaHO. Equivalent = 40.

200 grams. dissolved in water and diluted to one litre = 5N.

Ammonia (solution in water, NH_4HO). Equivalent = 35.

The strong solution, sp. gr. 0·880 = 20N. One volume of the strong solution diluted with 3 volumes of water = 5N.

Ammonium sulphide, $(NH_4)_2S$. Equivalent = 34.

600 c.c. of 5N ammonia are saturated with sulphuretted hydrogen; this gives hydrogen ammonium sulphide $H(NH_4)S$. This is made up to 1 litre by adding 5N ammonia. (This reagent is slowly decomposed by atmospheric oxygen, ammonia is evolved, and *yellow* ammonium sulphide is formed $(NH_4)_2S_2$.)

Sodium sulphide, Na_2S. Equivalent = 39.

200 grams of sodium hydroxide are dissolved in 800 c.c. of water.

400 c.c. of this solution are saturated with sulphuretted hydrogen, and the remaining half added, together with water sufficient to make the

* The system of standard reagents for use in qualitative analysis, upon which the instructions here given are based, was devised by Reddrop, and is published in full detail in the *Chemical News*, May, 1890. Mr. Reddrop employs the signature E (*equivalent*) instead of N (*normal*) in his system; but as the designation *normal* is the term almost universally employed for such solutions when used for *volumetric* analysis, it appears more harmonious, and brings qualitative analysis more into line with quantitative methods, to adopt a uniform nomenclature throughout.

† *Aqua regia* is prepared as required by mixing 1 volume of 16N nitric acid with 3 volumes of 10N hydrochloric acid.

volume up to 1 litre. When hydrogen sodium sulphide, HNaS, is required, the sodium hydroxide is simply saturated with sulphuretted hydrogen, without the further addition of sodium hydroxide.

Ammonium chloride, NH_4Cl. Equivalent = 53·5.

267·5 grams of the salt dissolved in water and diluted to one litre = 5N.

Ammonium carbonate,* $(NH_4)_2CO_3$. Equivalent = 48.

200 grams of ammonium sesquicarbonate (commercial carbonate) dissolved in 350 c.c. of 5N ammonia, and diluted with water to one litre = 5N.

Ammonium acetate, $(NH_4)C_2H_3O_2$. Equivalent = 77.

300 c.c. of glacial acetic acid (17N) neutralised with strong ammonia and diluted to one litre = 5N.

Reagents of Normal Strength. Signature N.

The following normal reagents are prepared by dissolving the equivalent weight in grams of the various salts in water, and diluting to one litre. In all cases the nearest whole number to the equivalent weight may be taken as sufficiently exact.

Ammonium sulphate, $(NH4)_2SO_4$.	Equivalent	weight	...	66·0
Barium chloride, $BaCl_2,2H_2O$.	,,	,,	...	122·0
Calcium chloride, $CaCl_2,6H_2O$.	,,	,,	...	109·5
Copper sulphate, $CuSO_4,5H_2O$.	,,	,,	..	124·75
Ferric chloride, $FeCl_3$.	,,	,,	...	54·17
Ferrous sulphate, $FeSO_4,7H_2O$.	,,	,,	...	139·0
Hydrogen disodium phosphate, $HNa_2PO_4,12H_2O$.	,,	,,	...	119·3
Lead acetate $Pb(C_2H_3O_2)_2,3H_2O$.	,,	,,	...	189·5
Lead nitrate, $Pb(NO_3)_2$.	,,	,,	...	165·5
Magnesium chloride, $MgCl_2,6H_2O$.	,,	,,	...	101·5
Magnesium sulphate, $MgSO_4,7H_2O$.	,,	,,	...	123·0

"Magnesia mixture" ($MgCl_2$, NH_4Cl, and NH_4HO).

68 grams of $MgCl_2,6H_2O$, together with 165 grams of NH_4Cl, are dissolved in 300 c.c. of water; 300 c.c. of 5N ammonia are added, and the solution diluted with water up to one litre.

Potassium chromate, K_2CrO_4.	Equivalent	weight	...	97·25
Potassium cyanide, KCy.	,,	,,	...	65·0
Potassium ferrocyanide, $K_4FeCy_6,3H_2O$.	,,	,,	...	105·5
Potassium ferricyanide, K_3FeCy_6.	,,	,,	...	109·7
Potassium sulphate, K_2SO_4.	,,	,,	...	87·0
Sodium acetate, $NaC_2H_3O_2,3H_2O$.	,,	,,	...	136·0

* Hydrogen ammonium carbonate, $H(NH_4)CO_3$, cannot be prepared stronger than 3N (see below).

Sodium acetate and acetic acid.

136 grams of the salt dissolved in 800 c.c. of water and 200 c.c. of glacial acetic acid added.

Sodium carbonate,* $Na_2CO_3,10H_2O$. Equivalent weight ... 143·0

Sodium thiosulphate, $Na_2S_2O_3,5H_2O$. Equivalent weight ... 124·0

Stannous chloride, $SnCl_2,2H_2O$. ,, ,, ... 112·5

112 grams of the salt are dissolved in 200 c.c. of 5N HCl, and the solution diluted with water to one litre. Fragments of granulated tin should be placed in the solution.

Reagents of Various Strengths.

Ammonium oxalate, $(NH_4)_2C_2O_4,2H_2O$. Equivalent weight ... 80·0

40 grams of the salt in one litre of water $= \frac{N}{2}$ solution.

Ammonium bicarbonate, $H(NH_4)CO_3$.

Saturation solution = 3N solution. Prepared by passing excess of CO_2 into 3N ammonia.

Ammonium thiocyanate, NH_4CyS. Equivalent weight ... 76·0

15 grams of the salt in one litre of water $= \frac{N}{5}$ solution.

Barium hydroxide, $Ba(HO)_2,8H_2O$. Equivalent weight ... 157·5

31 grams in one litre of water $= \frac{N}{5}$ solution.

Barium nitrate, $Ba(NO_3)_2$. Equivalent weight ... 130·5

65 grams dissolved in one litre of water $= \frac{N}{2}$ solution.

Bromine water, Br. Equivalent weight ... 80·0

Saturated solution, obtained by shaking up an excess of bromine with water. Gives a solution of $\frac{N}{2}$ strength.

Calcium hydroxide (lime-water) $Ca(HO)_2$. Equivalent weight ... 37·0

A saturated solution, obtained by shaking up an excess of lime with water and allowing the mixture to settle, = about $\frac{N}{20}$ solution.

Calcium sulphate, $CaSO_4$. Equivalent weight ... 66·0

A saturated solution, obtained by shaking up an excess of calcium sulphate with water, $= \frac{N}{30}$ solution.

Chlorine water, Cl. Equivalent weight ... 35·5

A saturated solution $= \frac{N}{5}$.

* A strong solution of sodium carbonate, 3N strength, should also be prepared by dissolving 429 grams of the salt in the litre. This is practically a saturated solution at ordinary temperatures.

Mercuric chloride, $HgCl_2$. Equivalent weight ... 135·5

27 grams dissolved in one litre of water $= \frac{N}{5}$ solution.

Mercurous nitrate, $Hg_2(NO_3)_2,2H_2O$. Equivalent weight ... 280·0

56 grams dissolved in 40 c.c. of 5N HNO_3 and diluted to one litre $= \frac{N}{5}$ solution. A small quantity of mercury should be placed in the bottle.

Potassium iodide, KI. Equivalent weight ... 166·0

33 grams dissolved in one litre of water $= \frac{N}{5}$ solution.

Potassium metantimoniate, $KSbO_3,3H_2O$. Equivalent weight ... 291·0

A saturated solution, obtained by shaking up an excess of the salt with water, $= \frac{N}{68}$

Silver nitrate, $AgNO_3$. Equivalent weight ... 170·0

3·4 grams dissolved in 100 c.c. $= \frac{N}{5}$ solution.

Fusion Mixture.—Pure anhydrous sodium and potassium carbonates are intimately mixed together in the proportion of their equivalent weights. Sodium carbonate 53 parts, and potassium carbonate 69 parts.

Table of Hardness.

Degrees of hardness expressed as parts of $CaCO_3$ per 100,000.

C.C. of soap solution.	$CaCO_3$ per 100,000 parts.	C.C. of soap solution.	$CaCO_3$ per 100,000 parts.	C.C. of soap solution.	$CaCO_3$ per 100,000 parts.	C.C. of soap solution.	$CaCO_3$ per 100,000 parts.
1·0	·48	5·0	6·00	9 0	11·80	13·0	18·02
·1	·63	·1	·14	·1	·95	·1	·17
·2	·79	·2	·29	·2	12·11	·2	·33
·3	·95	·3	·43	·3	·26	·3	·49
·4	1·11	·4	·57	·4	·41	·4	·65
·5	·27	·5	·71	·5	·56	·5	·81
·6	·43	·6	·86	·6	·71	·6	·97
·7	·56	·7	7·00	·7	·86	·7	19·13
·8	·69	·8	·14	·8	13·01	·8	·29
·9	·82	·9	·29	·9	·16	·9	·44
2·0	·95	6·0	·43	10·0	·31	14·0	·60
·1	2·08	·1	·57	·1	·46	·1	·76
·2	·21	·2	·71	·2	·61	·2	·92
·3	·34	·3	·86	·3	·76	·3	20·08
·4	·47	·4	8·00	·4	·91	·4	·24
·5	·60	·5	·14	·5	14·06	·5	·40
·6	·73	·6	·29	·6	·21	·6	·56
·7	·86	·7	·43	·7	·37	·7	·71
·8	·99	·8	·57	·8	·52	·8	·87
·9	3·12	·9	·71	·9	·68	·9	21·03
3·0	·25	7·0	·86	11·0	·84	15·0	·19
·1	·38	·1	9·00	·1	15·00	·1	·35
·2	·51	·2	·14	·2	·16	·2	·51
·3	·64	·3	·29	·3	·32	·3	·68
·4	·77	·4	·43	·4	·48	·4	·85
·5	·90	·5	·57	·5	·63	·5	22·02
·6	4·03	·6	·71	·6	·79	·6	·18
·7	·16	·7	·86	·7	·95	·7	·35
·8	·29	·8	10·00	·8	16·11	·8	·52
·9	·43	·9	·15	·9	·27	·9	·69
4·0	·57	8·0	·30	12·0	·43	16·0	·86
·1	·71	·1	·45	·1	·59		
·2	·86	·2	·60	·2	·75		
·3	5·00	·3	·75	·3	·90		
·4	·14	·4	·90	·4	17·06		
·5	·29	·5	11·05	·5	·22		
·6	·43	·6	·20	·6	·38		
·7	·57	·7	·35	·7	·54		
·8	·71	·8	·50	·8	·70		
·9	·86	·9	·65	·9	·86		

EXPANSION OF WATER BETWEEN 0° AND 25° C.

Temperature	Volume. (Vol. at 4° = 1.)	Density. (Density at 4° = 1.)
°		
0	1·00012	0·99988
2	1·00003	0·99997
4	1·00000	1·00000
6	1·00003	0·99997
8	1·00011	0·99989
10	1·00025	0·99975
12	1·00044	0·99956
13	1·00055	0·99945
14	1·00068	0·99932
15	1·00082	0·99918
15·5	1·00089	0·99911
16	1·00097	0·99903
17	1·00113	0·99887
18	1·00131	0·99869
19	1·00149	0·99851
20	1·00169	0·99831
22	1·00212	0·99787
24	1·00259	0·99742
25	1·00284	0·99717

The coefficients of expansion of water (the values in the middle column) between the temperatures 0° and 25° may be calculated from the formula—

$$V = V_0 - 0{\cdot}000061045t + 0{\cdot}000007718 3t^2 - 0{\cdot}000000037 34t^3$$

where V_0 = the volume at 0°. In the above table $V_0 = 1{\cdot}00012$; but if the coefficients are required when the volume at 0° is taken as unity, then $V_0 = 1$.

For temperatures above 25° a different formula is required.

TENSION OF AQUEOUS VAPOUR IN MILLIMETRES OF MERCURY.

For each fifth of a degree from 5° to 25° C.

°	mm.	°	mm.	°	mm.	°	mm.
5·0	6·5	10·0	9·2	15·0	12·7	20·0	17·4
·2	6·6	·2	9·3	·2	12·9	·2	17·6
·4	6 7	·4	9·4	·4	13·0	·4	17·8
·6	6·8	·6	9·5	·6	13·2	·6	18·0
·8	6 9	·8	9·7	·8	13·4	·8	18·3
6·0	7·0	11·0	9·8	16·0	13·5	21·0	18·5
·2	7·1	·2	9·9	·2	13 7	·2	18·7
·4	7·2	·4	10·1	·4	13·9	·4	19·0
·6	7·3	·6	10·2	·6	14·1	·6	19·2
·8	7·4	·8	10·3	·8	14·2	·8	19·4
7·0	7·5	12·0	10·5	17·0	14·4	22·0	19·7
·2	7·6	·2	10·6	·2	14·6	·2	19·9
·4	7·7	·4	10·7	·4	14·8	·4	20·1
·6	7·8	·6	10·9	·6	15·0	·6	20·4
·8	7 9	·8	11·0	·8	15·2	·8	20·6
8·0	8·0	13·0	11·2	18·0	15·4	23·0	20·9
·2	8·1	·2	11·3	·2	15·6	·2	21·1
·4	8·2	·4	11·5	·4	15·7	·4	21·4
·6	8·3	·6	11·6	·6	15·9	·6	21·7
·8	8·5	·8	11·8	·8	16·1	·8	21·9
9·0	8·6	14·0	11·9	19·0	16·3	24·0	22·2
·2	8·7	·2	12·1	·2	16·6	·2	22·5
·4	8·8	·4	12·2	·4	16·8	·4	22·7
·6	8·9	·6	12·4	·6	17·0	·6	23·0
·8	9·0	·8	12·5	·8	17·2	·8	23·3
						25·0	23·5

In cases where the tension rises 0·1 mm. for a rise of 0·2°, the pressure for the *intermediate* tenth degree may be taken as the same as that given for the temperature immediately preceding it. Thus, for the temperature 10·1°, the tension 9·2 mm. will be taken. For very accurate work, fuller tables given to the third decimal should be consulted.

Factors for reducing Gaseous Volumes to N.T.P.

The observed volume, when multiplied by the factor corresponding to the temperature and the pressure, will give the volume reduced to 0° and 760 mm. See footnote on p. 390.

mm.	9°.	10°.	11°.	12°.	13°.	14°.
720	·91711	·91388	·91066	·90746	·90426	·90113
1	·91839	·91515	·91192	·90872	·90552	·90238
2	·91966	·91642	·91318	·90998	·90677	·90363
3	·92093	·91769	·91445	·91124	·90803	·90488
4	·92221	·91896	·91571	·91250	·90929	·90614
5	·92348	·92023	·91698	·91376	·91054	·90739
6	·92476	·91150	·91824	·91502	·91180	·90864
7	·92603	·92277	·91951	·91628	·91305	·90989
8	·92730	·92403	·92077	·91754	·91431	·91114
9	·92858	·92530	·92204	·91880	·91556	·91239
730	·92985	·92657	·92330	·92006	·91682	·91365
1	·93112	·92784	·92457	·92132	·91808	·91490
2	·93240	·92911	·92583	·92258	·91933	·91615
3	·93367	·93038	·92710	·92384	·92059	·91740
4	·93495	·93165	·92836	·92510	·92184	·91865
5	·93622	·93292	·92963	·92636	·92310	·91990
6	·93749	·93419	·93089	·92762	·92436	·92115
7	·93877	·93546	·93216	·92888	·92561	·92241
8	·94004	·93673	·93342	·93014	·92687	·92366
9	·94132	·93800	·93469	·93141	·92812	·92491
740	·94259	·93927	·93595	·93267	·92938	·92616
1	·94386	·94054	·93722	·93393	·93064	·92741
2	·94514	·94180	·93848	·93519	·93189	·92866
3	·94641	·94307	·93975	·93645	·93315	·92992
4	·94768	·94434	·94101	·93771	·93440	·93117
5	·94896	·94561	·94228	·93897	·93566	·93242
6	·95023	·94688	·94354	·94023	·93692	·93367
7	·95151	·94815	·94480	·94149	·93817	·93492
8	·95278	·94942	·94607	·94275	·93943	·93617
9	·95405	·95069	·94733	·94401	·94068	·93742
750	·95533	·95196	·94860	·94527	·94194	·93868
1	·95660	·95323	·94986	·94653	·94319	·93993
2	·95788	·95450	·95113	·94779	·94445	·94118
3	·95915	·95577	·95239	·94905	·94571	·94243
4	·96042	·95704	·95366	·95031	·94696	·94368
5	·96170	·95831	·95492	·95157	·94822	·94493
6	·96297	·95958	·95619	·95283	·94947	·94619
7	·96424	·96084	·95745	·95409	·95073	·94744
8	·96552	·96211	·95872	·95535	·95199	·94869
9	·96679	·96338	·95998	·95661	·95324	·94994

mm.	9°.	10°.	11°.	12°.	13°.	14°.
760	·96806	·96465	·96125	·95787	·95450	·95119
1	·96934	·96592	·96251	·95913	·95575	·95244
2	·97061	·96719	·96378	·96039	·95701	·95370
3	·97189	·96846	·96504	·96165	·95827	·95495
4	·97316	·96973	·96631	·96291	·95952	·95620
5	·97443	·97100	·96757	·96417	·96078	·95745
6	·97571	·97227	·96884	·96543	·96203	·95870
7	·97698	·97354	·97010	·95670	·96329	·95995
8	·97825	·97481	·97137	·96796	·96455	·96120
9	·97953	·97608	·97263	·96922	·96580	·96246
770	·98080	·97734	·97390	·97048	·96706	·96371
1	·98208	·97861	·97516	·97174	·96831	·96496
2	·98335	·97988	·97642	·97300	·96957	·96621
3	·98462	·98115	·97769	·97426	·97083	·96746
4	·98590	·98242	·97895	·97552	·97208	·96871
5	·98717	·98369	·98022	·97678	·97334	·96997
6	·98844	·98496	·98148	·97804	·97459	·97122
7	·98972	·98623	·98275	·97930	·97585	·97247
8	·99099	·98750	·98401	·98056	·97710	·97372
9	·99227	·98877	·98528	·98182	·97836	·97497
780	·99354	·99004	·98654	·98308	·97962	·97622

mm.	15°.	16°.	17°.	18°.	19°.	20°.
720	·89800	·89489	·89180	·88873	·88569	·88266
1	·89924	·89613	·89304	·88997	·88692	·88389
2	·90050	·89737	·89428	·89120	·88815	·88511
3	·90174	·89862	·89551	·89243	·88938	·88634
4	·90299	·89986	·89675	·89367	·89061	·88757
5	·90423	·90110	·89799	·89490	·89184	·88879
6	·90548	·90234	·89923	·89614	·89307	·89002
7	·90673	·90359	·90047	·89737	·89430	·89124
8	·90798	·90483	·90171	·89861	·89553	·89247
9	·90922	·90607	·90295	·89984	·89676	·89369
730	·91047	·90732	·90418	·90107	·89799	·89492
1	·91172	·90856	·90542	·90231	·89922	·89615
2	·91296	·90980	·90666	·90354	·90045	·89737
3	·91421	·91104	·90790	·90478	·90168	·89860
4	·91546	·91229	·90914	·90601	·90291	·89982
5	·91671	·91353	·91038	·90725	·90414	·90105
0	·91795	·91477	·91162	·90848	·90537	·90228
7	·91920	·91602	·91285	·90971	·90660	·90350
8	·92045	·91726	·91409	·91095	·90784	·90473
9	·92169	·91850	·91533	·91218	·90907	·90594

mm.	15°.	16°.	17°.	18°.	19°.	20°.
740	·92294	·91975	·91657	·91342	·91030	·90718
1	·92419	·92099	·91781	·91465	·91153	·90841
2	·92544	·92223	·91905	·91589	·91276	·90963
3	·92668	·92347	·92029	·91712	·91399	·91086
4	·92793	·92472	·92152	·91836	·91522	·91208
5	·92918	·92596	·92276	·91959	·91645	·91331
6	·93043	·92720	·92400	·92082	·91768	·91454
7	·93167	·92845	·92524	·92206	·91891	·91576
8	·93292	·92969	·92648	·92329	·92014	·91699
9	·93417	·93093	·92772	·92453	·92137	·91821
750	·93541	·93217	·92896	·92576	·92260	·91944
1	·93666	·93342	·93020	·92700	·92383	·92067
2	·93791	·93466	·93143	·92823	·92506	·92189
3	·93916	·93590	·93267	·92946	·92629	·92312
4	·94040	·93715	·93391	·93070	·92752	·92434
5	·94165	·93839	·93515	·93193	·92875	·92557
6	·94290	·93963	·93639	·93317	·92998	·92679
7	·94414	·94087	·93763	·93440	·93121	·92802
8	·94539	·94212	·93887	·93564	·93244	·92925
9	·94664	·94336	·94010	·93687	·93367	·93047
760	·94789	·94460	·94134	·93811	·93489	·93170
1	·94913	·94585	·94258	·93934	·93613	·93292
2	·95038	·94709	·94382	·94057	·93736	·93415
3	·95163	·94833	·94506	·94181	·93859	·93538
4	·95288	·94957	·94630	·94304	·93982	·93660
5	·95412	·95082	·94754	·94428	·94105	·93783
6	·95537	·95206	·94877	·94551	·94228	·93905
7	·95662	·95330	·95001	·94675	·94351	·94028
8	·95786	·95455	·95125	·94798	·94474	·94151
9	·95911	·95579	·95249	·94921	·94597	·94273
770	·96036	·95703	·95373	·95045	·94720	·94396
1	·96161	·95827	·95497	·95168	·94843	·94518
2	·96285	·95952	·95621	·95292	·94966	·94641
3	·96410	·96076	·95744	·95415	·95089	·94764
4	·96535	·96200	·95868	·95539	·95212	·94886
5	·96659	·96325	·95992	·95662	·95335	·95009
6	·96784	·96449	·96116	·95785	·95458	·95131
7	·96909	·96573	·96240	·95909	·95581	·95254
8	·97034	·96698	·96364	·96032	·95704	·95376
9	·97158	·96822	·96488	·96156	·95827	·95499
780	·97283	·96946	·96611	·96279	·95950	·95622

mm.	21°.	22°.	23°.	mm.	21°.	22°.	23°.
720	·87972	·87668	·87371	751	·91759	·91442	·91133
1	·88094	·87790	·87493	2	·91882	·91564	·91254
2	·88216	·87911	·87614	3	·92004	·91686	·91376
3	·88339	·88033	·87735	4	·92126	·91808	·91497
4	·88460	·88155	·87857	5	·92248	·91929	·91618
5	·88583	·88277	·87978	6	·92370	·92051	·91740
6	·88705	·88398	·88099	7	·92492	·92173	·91861
7	·88827	·88520	·88221	8	·92615	·92295	·91982
8	·88949	·88642	·88342	9	·92737	·92416	·92104
9	·89071	·88764	·88463	760	·92859	·92538	·92225
730	·89193	·88885	·88585	1	·92981	·92660	·92346
1	·89316	·89007	·88706	2	·93103	·92782	·92468
2	·89438	·89129	·88827	3	·93226	·92904	·92589
3	·89560	·89251	·88949	4	·93348	·93025	·92711
4	·89682	·89372	·89070	5	·93470	·93147	·92832
5	·89804	·89494	·89191	6	·93592	·93269	·92953
6	·89927	·89616	·89313	7	·93714	·93391	·93075
7	·90049	·89738	·89434	8	·93836	·93512	·93196
8	·90171	·89860	·89555	9	·93959	·93634	·93317
9	·90293	·89981	·89677	770	·94081	·93756	·93439
740	·90415	·90103	·89798	1	·94203	·93878	·93560
1	·90538	·90225	·89920	2	·94325	·93999	·93681
2	·90660	·90347	·90041	3	·94447	·94121	·93803
3	·90782	·90468	·90162	4	·94570	·94243	·93924
4	·90904	·90590	·90284	5	·94692	·94365	·94045
5	·91026	·90712	·90405	6	·94814	·94486	·94167
6	·91148	·90834	·90526	7	·94936	·94608	·94288
7	·91271	·90955	·90648	8	·95059	·94730	·94409
8	·91393	·91077	·90769	9	·95180	·94852	·94531
9	·91515	·91199	·90890	780	·95303	·94973	·94652
750	·91637	·91321	·91012				

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